PROCESS ENGINEERING FOR LIGNIN VALUE PRIOR TO PULPING

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PROCESS ENGINEERING FOR
LIGNIN VALUE PRIOR TO PULPING

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To my grandparents

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LIST OF SYMBOLS AND ABBREVIATIONS

1-MI	1-methylimidazole
AFEX	Ammonia Fiber Expansion
APPTI	The Alliance for Pulp & Paper Technology Innovation
ATR-IR	Attenuated total reflectance infrared spectroscopy
B_{max}	Maximum Bound Dye
C_{BT}	Distillation base cost
C_P	Distillation total purchasing cost
C_{PL}	Distillation platform and ladder cost
C_T	Distillation tray cost
DB1	Direct Blue 1
DI Water	Deionized water
DLS	Dynamic light scattering
DMSO	Dimethyl sulfoxide
DO15	Direct Orange 15
DSTWU	Shortcut distillation design in ASPEN+
DY11	Direct Yellow 11
EG	Ethylene Glycol
E_T	Distillation tray efficiency
F_{NT}	Distillation number of trays
FPU	Filter-paper units
F_{TM}	Distillation material of construction
F_{TT}	Distillation tray type
GBL	γ-butyrolactone

GPC	Gel permeation chromatography
GVL	γ-valerolactone
HMDA	1,6 Hexamethylenediamine
HMW	High Molecular Weight
HSQC-NMR	Heteronuclear single quantum coherence spectroscopy
LMW	Low Molecular Weight
LP Steam	Low pressure steam (50 psig)
LVPP	Lignin Value Prior to Pulping
MP Steam	Medium pressure steam (150 psig)
NMP	N-methyl-2-pyrrolidone
NMR	Nuclear magnetic resonance
NREL	National Renewable Energy Laboratory
NRTL	Non-random two-liquid model
PG	Propylene glycol
PIXE	Proton induced X-ray Emission
RadFrac	Rigorous distillation design in ASPEN+
RBI	Renewable Bioproducts Institute
R_{min}	Minimum reflux ratio
SE	Steam Explosion
SEB	Steam Exploded Bagasse
SELP	Steam Exploded Loblolly Pine
TAPPI	Technical Association of the Pulp and Paper Industry
THF	Tetrahydrofuran
UNIFAC	UNIQUAC Functional-group Activity Coefficients
VPP	Value Prior to Pulping

SUMMARY

Biomass pretreatment unlocks chemical moieties for downstream valorization. This thesis focuses on organic solvent pretreatments that complement pulp production by delivering an additional lignin stream for the production of renewable chemicals. This work proposes and assesses a next-generation pulping process named Lignin Value Prior to Pulping (LVPP). Building off a foundation of organic solvent chemical pretreatments, this work develops tools to measure treatment efficacy, ranks solvents for LVPP, and describes the process of retrofitting a pulp mill. Together, this work creates a foundation for a two-step process to fully utilize both lignin and pulp streams. By incorporating an integrated computational and experimental technique, this thesis selects several effective chemical pretreatments given process-driven constraints.

This thesis accomplishes three objectives: Objective 1, develop an alternative measurement technique for cellulose accessibility to compare organic solvents and enhance a cellulose conversion rate model; Objective 2, employ chemical properties and rapid tests to establish a solvent selection methodology for LVPP; and Objective 3, integrate process and cost models to assess the feasibility of LVPP and required lignin selling price.

In CHAPTER 2, this work presents Direct Yellow 11 as a replacement for Direct Orange 15 for Simons' staining. This new measurement probe outperforms the previous probe in all tests and provides lignocellulosic accessibility data for a wide range of organic solvents. CHAPTER 3 details two performance screens for LVPP and definitively shows that solubility of an industrial lignin in organic solvents does not directly correlate to delignification efficacy. CHAPTER 4 presents a complete LVPP scenario that uses a

treatment of 1,6 hexamethylenediamine. A techno-economic analysis presents a lignin selling price of $0.829/kg for economic viability. This chapter also highlights the key unit operations and assumptions that govern LVPP feasibility. Within the LVPP process, a key unit operation is the separation of lignin, solvent, and water. Water precipitation, a method to separate lignin and water, is explored in CHAPTER 5, and a quick economic screen is developed to compare organic solvent treatments. The high liquid volumes required for water precipitation lead to separation costs greater than $1.50/kg lignin and will require the development of new separation techniques. Finally, CHAPTER 6 evaluates a set of solvents by a thorough selection methodology for LVPP that is based on hazard, exposure, efficacy, and economic principles. A screen of 30 organic solvents presents a subset of recommended solvents that includes 1,6 hexamethylenediamine, diethanolamine, propylene glycol, and 1-methyl piperazine. Each of these solvents should be further investigated for LVPP.

This thesis aids the diversification of the pulp and paper industry towards new products. It presents process and cost models that highlight feasibility constraints and technological barriers to future LVPP process viability. In addition to these obstacles, this thesis explores the lignin valorization potential of LVPP and the downstream pulp mill enhancements. By utilizing a higher percentage of the original biomass feedstock for high value products, this work pushes the field towards more favorable economics for renewable chemicals.

CHAPTER 1. INTRODUCTION

1.1 Biomass overview

Fossil fuels and their derivatives are society's principal sources for energy, chemicals, and materials. These finite resources have bolstered industrialization and economic growth over the past century, but decades of over-use have led to negative changes in both our environment and our future resources. Thirty-two years ago, in a review of human activity, the United Nations declared that humanity "borrows environmental capital from future generations with no intention or prospect of repaying" (Brundtland 1987). Society has responded by promoting sustainability initiatives that answer the call to "meet the needs of the present without compromising the ability of future generations to meet their own needs" (Brundtland 1987).

This response has led to our ability to harness energy from the sun, the wind, and the water. It has also driven trillions of dollars in funding for bio-based energy and chemicals (McBride 2015). Global biomass takes in approximately 100 terawatts of energy through photosynthesis (Taylor 2012) and stores this energy in carbon rich polymers. Accessing this energy is a key task of the 21st century to reach sustainability goals and reduce our dependence on fossil fuels.

1.2 Biomass Components

Plants come in all shapes and sizes, but they all contain three carbon rich polymers: cellulose, hemicellulose, and lignin. These polymers form a strong network to reinforce the cell wall and provide the plant with resistance and protection from outside stresses (Ochoa-Villarreal, Aispuro-Hernández et al. 2012). Each polymer has a unique set of chemical

moieties that store energy from the sun. An atom efficient way to access stored energy is through utilization of these aliphatic and aromatic moieties in the production of chemicals or materials.

1.2.1 Lignin

Lignin consists of cross-linked phenolic groups. As the only large-scale source of natural aromatics, lignin's potential value has sparked interest for centuries. From the pulp and paper industry to biofuels, advances in chemical synthesis are providing new routes for lignin valorization (Ragauskas, Beckham et al. 2014). However, this valorization is tempered by extraction and chemical processing difficulties. As a complex polymer that is composed of three phenolic monomers, paracoumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (Thakur, Thakur et al. 2014), extracted lignin varies in chemical composition from plant to plant. This heterogeneity creates many downstream processing challenges, especially in the production of renewable chemicals and fuels. Lignin's role in the plant is to protect the fibers while providing strength, rigidity, and degradation resistance to plants (Davis, Tao et al. 2013). Fully incorporated into each plant, the difficulty of lignin extraction has required harsh treatments that remove important chemical moieties and lead to processes that resort to burning lignin for energy. In the pulp and paper industry alone, over 65 million tons of lignin are burned annually (FAOSTAT 2018). Lignin has a high heat of combustion (28.5 MJ/kg), but the cost of replacing that energy with natural gas amounts to just $80/metric ton. To better utilize this natural resource, an understanding of biomass pretreatment and processing is required.

1.2.2 Cellulose

Cellulose, the most abundant renewable polymer, is comprised of linear, non-branched chains of $\beta_{1,4}$ linked D-glucose. The cellulose chains aggregate with strong intermolecular bonds and form compact, highly-ordered microfibrils. As a homogeneous polymer, cellulose is more easily converted into renewable chemicals and fuels. Once isolated, cellulose strands can be synergistically degraded into glucose by three types of cellulases: endoglucanases, cellobiohydrolases, and β-glucosidases. These enzymes randomly cleave $\beta_{1,4}$-glycosidic bonds on cellulose chains, form cellobiose by attacking from chain ends, and convert cellobiose to glucose respectively (Henrissat 1994, Rabinovich, Melnick et al. 2002). The cost of enzymes and biomass processing, along with low oil prices, have weakened the value propositions of using cellulose as a feedstock for biofuels. However, the long cellulosic fibers in most biomass make it perfectly suited for pulp and paper products. Stoichiometrically, a kg of cellulose (glucose) can be converted to 0.511 kg of ethanol and 0.489 kg of carbon dioxide. An ethanol price of $0.428/kg and a pulp price of $0.875/kg makes ethanol from cellulose four times less valuable than pulp from cellulose. Comparing the margins for renewables from lignin and cellulose, it is clear that lignin has a greater economic potential in this space.

1.2.3 Hemicellulose

The last major component of biomass is hemicellulose, which exists as a branched and esterified polysaccharide composed of simple sugars linked by glycosidic bonds (Donohoe, Decker et al. 2008, Yarbrough, Himmel et al. 2009). This low molecular weight polysaccharide consists of both C5 and C6 sugars that interact with both cellulose and lignin to protect the cell wall. These interactions prevent direct contact among cellulose

microfibrils and create additional barriers for enzymatic degradation (Ogiwara and Arai 1968, Wallace, Chesson et al. 1991). Hemicellulose is the easiest component to extract, and its utilization has taken the form of ethanol production (Nigam 2001), hydrogen reforming (Czernik, French et al. 2002), and combustion among others (Dorez, Ferry et al. 2014).

1.3 Biomass Fractionation

Lignocellulosic biomass fractionation is limited by the intramolecular strength of each polymer, the strong intermolecular interactions between the polymers, and the physical hierarchy into which the components are assembled. The term for this resistance is recalcitrance, and it is largely responsible for the high processing costs of cellulosic material (Himmel, Ding et al. 2007). This high recalcitrance requires a pretreatment unit operation to prepare biomass for downstream applications. Two major industries have tackled this challenge with different product targets. The pulp and paper industry focuses on the separation of lignin while maintaining the carbohydrate fibers. In contrast, the biofuels industry focuses on separating lignin while breaking down the carbohydrates (Santos, Hart et al. 2013). Towards obtaining value from lignin, it is valuable to understand the different biomass treatment methods. To date, there have been many published pretreatment methods for a multitude of substrates. These pretreatment techniques can generally be grouped into four categories: biological, physical, physiochemical, and chemical pretreatments.

1.3.1 Biological Pretreatments

Biological pretreatments typically use wood-degrading rot fungi to prepare lignocellulosics for enzymatic degradation. The most studied biological pretreatment

agents are white and brown rot fungi (Worrall, Anagnost et al. 1997). These fungi do not require high costs, however they provide little lignin degradation (Kim and Newman 1995, Goodell, Nicholas et al. 2001). Despite their low energy and capital costs, biological pretreatment methods are limited by slow digestion rates and low selectivity (Lee, Gwak et al. 2007).

1.3.2 Physical Pretreatments

Physical pretreatments decrease the particle size of biomass to increase the surface area for pulp bonding or for enzymes to adsorb onto the surface. Mechanical pulping is a high yield process that produces weak fibers often used in newspaper and other low strength products. Ball milling, the most prevalent physical pretreatment for renewable chemicals, reduces typical particle size to 0.2 mm and may be combined with other pretreatment methods to achieve greater effect (Kumar, Barrett et al. 2009). The main drawback to ball-milling is that it requires large quantities of energy, has high industrialization costs, and does not remove lignin.

1.3.3 Physiochemical Pretreatments

Physiochemical pretreatments both decrease the particle size of biomass and chemically modify the lignocellulosics. The two main techniques are steam explosion (SE) and ammonia fiber expansion (AFEX). SE uses a quick pressure drop to explode biomass with hot, pressurized water. Its efficiency and processing are highly substrate dependent and require acid catalysts for high efficacies on woody biomass (Brownell, Yu et al. 1986, Kaar, Gutierrez et al. 1998). While beneficial for biofuels, SE disrupts the fibril structure sufficiently well that it is not compatible with pulping processes. AFEX has the same mechanism of action as SE but uses more moderate conditions (Alizadeh, Teymouri et al.

2005, Zheng, Pan et al. 2009). Liquid, anhydrous ammonia is exploded by a sudden pressure drop to disrupt the cellulose crystal structure and enhance enzymatic hydrolysis (Kumar, Barrett et al. 2009). AFEX is more efficient than SE for agricultural residues with low lignin content (Cantarella, Cantarella et al. 2004), but AFEX is ineffective for pulping due to its low efficacy on high-lignin, woody biomass (Chundawat, Vismeh et al. 2010).

1.3.4 Chemical Pretreatments

Chemical pretreatments are the broadest and fastest growing of all the pretreatment techniques. The earliest industrialized pretreatments are acid and alkali pretreatments. More recently, organic solvents have come into vogue in the form of pure solvents, ionic liquids, and deep eutectic solvents. The application of these solvents is primarily focused on the fractionation of biomass into its three main components (da Costa Sousa, Chundawat et al. 2009). Some promising chemical pretreatments are presented in Table 1.

Table 1. Promising chemical pretreatment technologies.

Chemical Pretreatment	Operating Conditions	Disadvantages
Acid	Dilute or concentrated: High temperatures	Fiber degradation, solvent recovery
Alkali	Moderate conditions	Slow rates, low selectivity
Ionic Liquids	Moderate conditions	High costs, recovery
Deep Eutectic Solvents	Moderate conditions	Low efficacy
Pure Organic Solvents	High temperatures	Recovery and efficacy

1.3.4.1 Acid Treatment

Acid pretreatments were forerunners in both the pulp and biofuels industries. Acid sulfite pulping was introduced in 1857 and was the dominant biomass process in the early 1900s (Roth 1857, Richter 1932). Similarly, dilute acid pretreatment was the leading candidate for renewable chemical production (Grohmann, Torget et al. 1986). Touted for its low costs and high efficiencies, dilute acid was implemented in pilot plants with limited success (Schell, Farmer et al. 2003, Lynd, Liang et al. 2017). Dilute acid pretreatment releases hemicellulose and increases the biomass void volume for enzymatic attack. However, solvent recovery and weakened pulp are two key limitations to acidic treatments.

1.3.4.2 Alkali Treatment

Alkali pretreatment uses sodium hydroxide and lime (calcium hydroxide) to alter the biomass structure (Gould 1984). Alkali dissolves lignin and hemicellulose to expose the cellulose and increase cellulose accessibility to hydrolytic enzymes (Zheng, Pan et al. 2009). These inexpensive pretreatments require extended periods of time for efficacy, but they can be performed at high or low temperatures and pressures (Mosier, Wyman et al. 2005). As the predominant pulping process, alkali treatment of biomass is cost effective. However, high severity and the addition of sulfide is required for woody biomass treatments with high throughputs (Dahl 1884). While currently feasible, the economics of alkali pretreatments are limited due to the low-quality lignin and reduced selectivity towards lignin. Due to its harsh conditions, alkaline treated lignin is highly condensed and less suitable for renewable chemicals (Kondo and McCarthy 1985). Condensed lignin has more carbon-carbon interunit linkages than native lignin.

1.3.4.3 Ionic Liquids and Deep Eutectic Solvents

Ionic liquids and deep eutectic solvents are both liquids that resulted from the mixture of solid chemicals. Ionic liquids are molten organic salts, generally liquid below 100°C (Gericke, Fardim et al. 2012), can be bio-derived, and many are considered green solvents (Tadesse and Luque 2011). Deep eutectic solvents are formed by a eutectic mixture of Lewis or Brønsted acids and bases with a variety of anionic and/or cationic species (Smith, Abbott et al. 2014). The first cellulose dissolution in an ionic liquid was demonstrated with an imidazolium based cation in 2002 (Swatloski, Spear et al. 2002). Deep eutectic solvents have also provided enzymatic hydrolysis enhancements for biomass and aid in fractionation (Procentese, Johnson et al. 2015). As chemical pretreatments for biofuels, ionic liquids and deep eutectic solvents pose inhibition problems for downstream hydrolysis and are historically expensive and hard to recover. New pretreatments are reducing these costs (George, Brandt et al. 2015), but the solubilization and disruption of cellulose microfibrils is a technological barrier for pulp production.

1.3.4.4 Organic Solvents

Many individual organic solvents have shown significant success as pretreatment methods in pulping and in renewable chemical production. Pulping with organic solvents has been reviewed extensively since its introduction (Johansson, Aaltonen et al. 1987, Rodríguez and Jiménez 2008). From amines to alcohols, organic solvents have demonstrated an ability to remove a higher quality lignin than Kraft pulping. The quality of pulp varies from solvent to solvent, but a common challenge is shortened fibers, yield losses, or bleaching (Julien and Malcolm 1978, Rodríguez and Jiménez 2008). For many solvents, the additional requirement of acid catalyst leads to a weakened pulp and full

removal of hemicellulose. Particularly for softwood treatment, only a handful of tests have explored an uncatalyzed treatment (Lesar, Humar et al. 2016). In addition to solvent efficacy, solvent recovery is the major process challenge for organic solvent pulping (Zhao, Cheng et al. 2009, Viell, Harwardt et al. 2013).

An additional set of solvents have been explored in biomass fractionation for renewable chemicals. Monoethanolamine and several γ-lactones were shown to dissolve lignin and yield cellulose-rich solids (Claus, Kordsachia et al. 2004, Petrus and Petrus-Hoogenbosch 2007). One of these γ-lactones, γ-valerolactone (GVL), was further explored as an effective green solvent that can be derived from cellulose (Luterbacher, Rand et al. 2014). GVL may be used individually as a pretreatment for enzymatic hydrolysis or combined with dilute acid for the non-enzymatic production of sugar (Shuai, Questell-Santiago et al. 2016). An additional co-solvent system using tetrahydrofuran (THF) produces various hydrocarbon fuels from woody biomass (Cai, Zhang et al. 2013). A similar solvent to THF, 2-methyltetrahydrofuran (2-methyl THF), may be used in a biphasic system with water that fractionates lignin, hemicellulose, and cellulose (vom Stein, Grande et al. 2011). 1-methylimidazole (1-MI) is a precursor to imidazolium-based ionic liquids and an efficient delignifier for many pretreated lignocellulosics (Kang, Realff et al. 2015). These solvents represent a minute fraction of the overall solvent space, but their success provides valuable insight into solvent characteristics that enable biomass fractionation.

1.4 Biomass Processing

Biomass fractionation is only one step in a chemical process to produce renewable chemicals or materials. Other steps include, but are not limited to, solid handling, solid

washing, solvent separation, solvent regeneration, depolymerization, and polymer modification. The implementation of these steps is highly dependent on the final product, the feedstock, and the treatment chemicals. Nevertheless, techno-economic analyses of biomass processes may be utilized to direct the application of different unit operations.

1.4.1 Techno-economics of Biomass Processes

The economic feasibility of a process is a key indicator of its future funding and success. This postulate can apply to the process as a whole, or to a unit operation within the process. Integrated into the economics of biofuel or renewable chemical processes are the pretreatment and fractionation unit operations. These steps are the most expensive processing steps, and they account for more than 20% of the total processing cost, including feedstocks (Humbird, Davis et al. 2011). Thus, it is of great importance to find pretreatment solvents with the highest economic viability. Towards economic optimization, this search involves designing a process flowsheet, analyzing the economics of inputs and outputs, and then determining governing equations for each unit operation.

Techno-economic analyses are increasingly common for the pretreatment of lignocellulosics for bioethanol production. Processes including ethanol treatment (Kautto, Realff et al. 2014), dilute acid (Kazi, Fortman et al. 2010), ionic liquids (Klein‐Marcuschamer, Simmons et al. 2011), and steam explosion (Shafiei, Kabir et al. 2013) have been well studied with techno-economic analysis. These analyses highlight four key unit operations within a biomass treatment process, (1) the dissolution of lignin, (2) cellulose enhancement, (3) required washing, and (4) solvent recovery from lignin. However, analysis of most organic solvent pretreatment methods does not include techno-

economic analysis. Many organic solvent pretreatment methods are at low technology readiness levels and process considerations are often left for future work.

1.4.2 Process Design

In conjunction with a techno-economic analysis, process design and innovation are key to maximizing profitability. For each of the four key unit operations outlined in the previous section, multiple process configurations have been proposed. The chemicals used to extract lignin are reviewed in SECTION 1.3 of this work. These chemicals have been applied to biomass in both stirred tank reactors (Ropars, Marchal et al. 1992) and plug flow digesters (Richter and Richter 1965). Similarly, cellulose enhancement can take place in a fermenter (Brethauer and Wyman 2010) or in a refiner (Gharehkhani, Sadeghinezhad et al. 2015); solid washing can occur in a rotary drum (Dinwiddie 1938) or on a conveyer belt (Thomas 1982); and lignin precipitation can utilize acids, gasses, liquid-liquid extractions, or temperature swings. Solvent separation processes are critical unit operations in all industries and can take the form of evaporators, membranes, or distillation columns (Chrisandina, Kwok et al. 2019). Process design considerations must be based in both scientific understanding and techno-economic evaluations. Together these components facilitate the effective implementation of complex process designs.

1.5 Lignin Value Prior to Pulping

A survey of biomass pretreatment highlights the dichotomy between the Kraft process and organic solvent fractionation of biomass. On one hand, a severe alkali treatment leads to low quality lignin and high-quality pulp. On the other hand, certain

organic solvents yield selective removal of high-quality lignin but result in poor fiber quality. Lignin value prior to pulping (LVPP) seeks to bridge this divide to improve the lignin stream and the pulp stream in a pulp mill. This two-step treatment selectively removes a fraction of biomass lignin in a pretreatment step and then produces pulp from the delignified biomass. Founded on the retention of cellulose for pulp, LVPP utilizes knowledge from the biofuels industry but may be considered a next-generation Kraft pulp mill. By modifying the existing assets of a Kraft pulp mill, LVPP enables a smaller investment of capital than a new biorefinery that caters to a larger fuels market.

1.5.1 Kraft Pulp Mills

With an extensive infrastructure of Kraft pulp mills, the United States pulp and paper industry is poised to take advantage of the scientific breakthroughs in lignocellulosic treatments. The mass value of pulp is double that of fermentable sugars, and pulp yields are higher than sugar yields per ton of cellulose. Thus, from an economic perspective, woody cellulose is best positioned towards pulp and paper products unless current fuel prices rise substantially. While recycled fibers are the feed for the majority of pulp products, an estimated 66 million tons of wood pulp was produced in the United States in 2016 (FAOSTAT 2018). The overwhelming majority of wood pulp is produced through the Kraft pulping process.

Developed initially by Carl F. Dahl in 1879, the Kraft process became ubiquitous after the development of the recovery boiler by G.H. Tomlinson in the 1930s. Wood chips are impregnated with steam in a vessel, cooked in a pressurized digester with NaOH and Na_2S, blown into a collection tank, screened by a combination of sieves and centrifuges, washed in rotary drums, and then bleached in vessels. The chemicals used to cook the

chips, termed white liquor, are recycled by a series of evaporators, a recovery boiler and a lime kiln. This chemical recycling is essential for an economic process, and pulping chemicals are recycled at an average of 97% (Tran and Vakkilainen 2008).

Kraft processes can process both hardwoods and softwoods and produce many grades of fibers. Pulp yields range from 50% for corrugated to 45% for bleached grade (Smook 1992). The largest capital cost in the pulping process is the recovery boiler (Brewster 2007) and the largest energy cost is the multi-effect evaporator chain (Kautto, Saukkonen et al. 2010). The load to the recovery boiler is determined by the rate of lignin, and to some extent the rate of hemicellulose, removed from the biomass. The evaporator energy demand is determined by the amount of water required to wash the solids.

Simply put, the Kraft process is a chemical process that removes lignin to create pulp and burns the residual solids to recover treatment chemicals. As detailed in SECTION 1.2.1, the energy value of burning lignin is just $80/metric ton. Since only 50% of a Kraft pulp mill's feedstock is converted to a high value product, many attempts have been made to better utilize the majority of biomass.

1.5.2 Prior Modifications to Kraft Pulp Mills

Most of these Kraft pulp mill improvements have revolved around engineering and equipment rather than chemical changes (Blain 1993). However, there are several improvements that have focused on new products and new chemistries (Courchene 1998). These modifications have been attempted to varying degrees of success.

Three notable modifications target the effectiveness of the digester treatment. The first is a process modification that utilizes low pressure steam to heat the wood chips and

drive out entrained air pockets. This pretreatment is now common in continuous digesters and decreases the required cook time by improving impregnation (Marcoccia, Prough et al. 1999). Two additive chemicals have also been explored to improve the Kraft process. In 1977, anthraquinone was introduced as a synergistic catalyst that improved the treatment of woodchips in the digester (Holton 1977). Easily added into an existing process, anthraquinone decreased the residual lignin content while maintaining yield at constant cooking conditions (Blain 1993). While widespread following its inception, carcinogenicity studies derailed its implementation (Hart and Rudie 2014). Another additive, sodium borohydride, is a reducing agent that increased the rate of delignification and increased pulp yield (Hartler 1959).

Additional process modifications have targeted the non-cellulosic feedstock components. Process modifications were initiated to create value from the extractives of softwood that naturally produce tall oils. Skimming tanks were implemented and tall oil accounts for at least 1% of revenue for most softwood Kraft processes (Norlin 2000). To better utilize lignin, several pulp mills have adopted a lignin precipitation step following extraction from the wood chips. By removing lignin without burning it, processes like LignoBoost and LignoForce are able to reduce the load to their boilers while producing a lignin stream (Tomani 2010, Kouisni, Holt-Hindle et al. 2012). However, as described in SECTION 1.3.4.2. the alkali treatment results in a low-quality Kraft lignin that is highly condensed and sulfur containing. A final enabling technology that was proposed but not implemented is value prior to pulping (VPP) with a focus on the extraction of hemicellulose for fermentation to biofuels (Van Heiningen 2006). The VPP process extracts hemicellulose that would typically dissolve into the black liquor and isolates it for production of polymers and other commodity chemicals that are much more valuable.

Viable hemicellulose streams and lower cooking times have been demonstrated in VPP studies (Al-Dajani, Tschirner et al. 2009, Helmerius, von Walter et al. 2010). However, techno-economic analysis has demonstrated the process' inability to overcome pulp yield losses of 5-15% (Duarte, Ramarao et al. 2011), and pulp quality degradation (Kautto, Saukkonen et al. 2010).

In this thesis, we present a modification to a Kraft pulp mill that addresses technical challenges encountered by previous modifications. By removing lignin prior to pulping, LVPP opens up three additional avenues for increased value: a lignin stream, increased pulp throughput, and an extended life for the recovery boiler.

1.6 Dissertation Map

This thesis work mainly focuses on the process development and solvent selection for LVPP. CHAPTER 2 presents a study of solvent treatment on steam-exploded bagasse (SEB) and a measurement tool to predict the accessibility of treated cellulose fibers. CHAPTER 3 explores the correlation between lignin solubility in a solvent and delignification of juvenile slash pine chips. CHAPTER 4 describes the process development and preliminary techno-economics of LVPP. CHAPTER 5 highlights the challenges of water precipitation for LVPP and compares three separation techniques. CHAPTER 6 presents a solvent selection methodology for LVPP. CHAPTER 7 summarizes the main findings of previous chapters and summarizes opportunities for future research and development.

CHAPTER 2. A PROBE FOR CELLULOSE ACCESSIBILITY

2.1 Introduction

Towards understanding the impact of biomass treatment, the accessibility, or availability of the β 1,4-glycosidic bonds in cellulose, has been studied extensively on both cellulosic and lignocellulosic substrates. To date, no single method has proven universal for absolute measurement of this complex physical property. Adsorption of cellulose binding modules and cellulase enzymes may be employed to directly measure accessibility (Gourlay, Arantes et al. 2012). However, these assays are expensive and difficult to perform on lignin-containing substrates due to competitive adsorption of the cellulase components on lignin. Additional techniques, such as high-resolution electron microscopy (White and Brown 1981), nitrogen adsorption (Chen, Wang et al. 2010), mercury porosimetry (Simitzis, Sfyrakis et al. 1995), solute exclusion (Stone, Scallan et al. 1969), and water retention are also used (Herrick, Casebier et al. 1983). These techniques each come with various drawbacks and benefits outlined in several review articles (Wang, He et al. 2012, Zhao, Zhang et al. 2012, Meng and Ragauskas 2014). Specifically, these techniques may be evaluated by their interactions with a lignocellulosic substrate and their ability to mimic the cellulose enzyme complexes (Luo and Zhu 2011). Simons' staining employs a set of specific dyes that selectively adsorb to cellulose, are applied to wet substrates, and have been reported to have a similar size profile to cellulase enzymes (Abuja, Schmuck et al. 1988, Chandra and Saddler 2012). These three characteristics render Simons' staining a highly attractive accessibility measurement technique that has been used in over 100 peer-reviewed articles over the last five years.

Simons pioneered the use of azo-stilbene dyes as lignocellulose probes to measure the micropores of beaten pulp (Simons 1950). Various modifications to Simons' staining protocol have been made to allow for faster screening and higher throughput (Chandra, Ewanick et al. 2008). One azo-stilbene dye, Direct Orange 15 (DO15), demonstrates a high affinity for cellulose and strong similarities to cellulase enzymes (Yu, Minor et al. 1995). Specifically, the high molecular weight fraction (HMW), retained behind a 100 kDa membrane, has a high affinity for cellulose and is reported to have a hydrodynamic diameter similar to that of cellulase enzymes. Thus, it has been proposed that HMW DO15 can be used alone as a surrogate for cellulase that selectively binds cellulose fibers over lignin (Chandra, Arantes et al. 2015). Pylam Products, the original distributor of DO15, has stopped formulating and selling DO15 for economic reasons. A similar azo-stilbene dye, Direct Yellow 11 (DY11) was recently proposed as an alternative dye for measuring accessibility (Zhang, Vancov et al. 2016).

DY11 is shown to correlate with enzymatic hydrolysis over a variety of different substrates (Zhang, Vancov et al. 2016). We present additional characterization of DY11, specifically a comparison between DY11 and DO15, to demonstrate that it may be used as an alternative to DO15 in future Simons' staining applications.

As demonstrated in Figure 1, both DY11 and DO15 are condensation products of 5-nitro-o-toluenesulfonic acid, and this structural homology should lead to similar functionality (Smith 2000). The present work compares these two dyes to determine if DY11 is as effective as DO15 at measuring lignocellulosic accessibility.

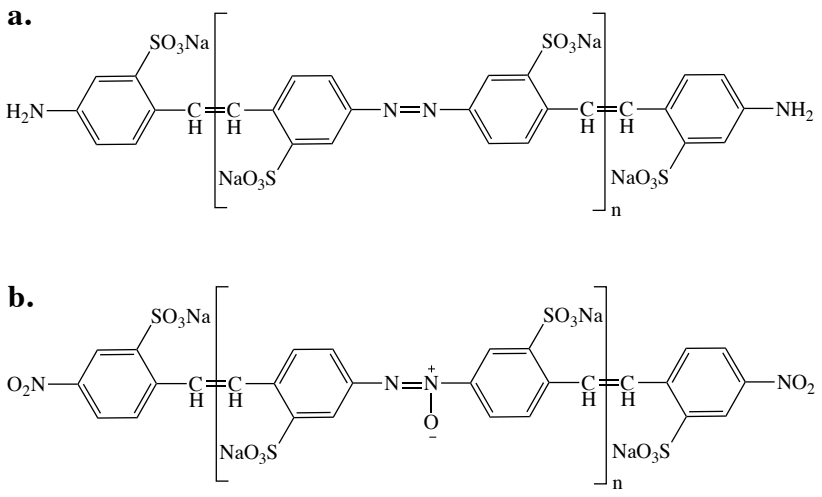


Figure 1. Published structures of azo-stilbene dyes. (a) DO15: Color index 40002/3 and (b) DY11: Color index 40000 (Smith 2000).

Specifically, we compare dye adsorptions to a full range of substrates, define and characterize a dye fractionation procedure, analyze dye absorption spectra, and check the correlation of dye adsorption to cellulose conversion rates. We use DY11 in an adsorption screen to compare organic solvents and quantify their impact on steam exploded bagasse (SEB). This efficacy is further compared against wood chip delignification efficacy.

2.2 Materials and Methods

2.2.1 Substrates

Avicel PH-101 (11365) and Fibrous Cellulose (C6288, medium) purchased from Sigma-Aldrich (St. Louis, MO, USA) were used as model cellulosic substrates. Organosolv lignin (371017) from Sigma-Aldrich was used as a model lignin. EtOH-soluble lignin was provided by American Process Inc. (Atlanta, GA). SEB, a sugar cane bagasse pretreated with 2.5% SO_2 and steam exploded at 200˚C for 5 minutes, was provided by Dr. Guido

Zacchi at the University of Lund, (Lund, Sweden). Steam-exploded loblolly pine (SELP) samples were provided by Dr. John Muzzy at the Georgia Institute of Technology (Atlanta, GA). These steam-exploded samples were used as a basis for this work's lignocellulosic studies. The Chemical Analysis Group of the Renewable Bioproducts Institute provided compositional analysis for the substrates (APPENDIX A.2). Both substrates are primarily composed of glucan and acid-insoluble lignin with negligible hemicellulose content.

2.2.2 Pretreatment

1-MI (99%) and Phosphoric Acid (85%) were purchased from Sigma Aldrich and EMD Bioscience (Gibbstown, NJ, USA) respectively. Phosphoric acid treatment of lignocellulosic substrates was performed according to the procedure described by (Hall, Bansal et al. 2010). 30 grams of diluted ice-cold phosphoric acid was used to pretreat 1 gram of slightly hydrated substrate for 40 minutes with occasional stirring. 20 mL of ice-cold acetone was used for regeneration of cellulose. The resulting solid was washed three times with 20 mL ice-cold acetone, and four times with 100 mL DI water. The washed solid fraction was subsequently used for adsorption and hydrolysis reactions.

Additional organic solvents were purchased through VWR International (Radnor, PA). Pretreatments were performed at solid loadings of 40 mg/mL at 40˚C for 30 minutes with vigorous shaking. The solid substrate was washed with eight volume equivalents of DI water prior to enzymatic hydrolysis. All pretreatments demonstrated a negligible amount of cellulose loss. Therefore, we assumed a constant glucose fraction, and additional compositional analyses were not performed after pretreatment.

2.2.3 Delignification

Klason lignin was determined by a modified version of NREL's Determination of Structural Carbohydrates and Lignin in Biomass (Sluiter, Hames et al. 2008). Dry, milled (0.84 mm screen) samples (0.175 ± 0.005 g) were weighed in flat-bottomed tubes, and 1.5 mL of 72% v/v sulfuric acid (VWR North America, Radnor, PA) was subsequently added. The tubes were placed into a Digiblock digital block heater (Sigma-Aldrich, St. Louis, MO) to maintain the temperature at 30 °C and stirred every 3 to 5 min for 1 h. Each sample was diluted to 42 mL, autoclaved for 2 h at 121 °C, and cooled to room temperature. The samples were filtered by G8 glass filters and the remaining solids were dried at 105 °C to determine Klason lignin content. The Klason lignin content was determined gravimetrically as a fraction of the initial biomass.

2.2.4 Simons' Staining

DO15 and DY11 dyes were obtained from Pylam Products (Garden City, NY). Direct Blue 1 (DB1, CAS 2610-05-1) was obtained from Sigma Aldrich. HMW fractions of DO15 and DY11 were isolated (Chandra, Ewanick et al. 2008). DI water was added to dyes to yield 10 mg/mL stock solutions. Two levels of filtration with 100 kDa and 10 kDa polyethersulfone membranes were performed in series to yield three dye fractions. Each level of filtration was employed at least three times (APPENDIX A.2).

A modified Simons' staining procedure was scaled down by a factor of 10 to a total volume of 1.0 mL (Chandra and Saddler 2012). In short, 10 mg of substrate were weighed into tubes and mixed with the required amount of water and a phosphate buffer (140 mM NaCl, 0.3M Phosphate, pH 6.0). Increasing amounts of dyes were allowed to adsorb for 6 hours at 70˚C with moderate shaking. Free dye was measured using a spectrophotometer

(DU 800 Beckman Coulter). Extinction coefficients for free dye measurements were calculated for each dye batch. Adsorbed, or bound dye was calculated by subtraction. The maximum bound dye was designated, B_{max}. For DY11 and DO15 on 10 mg samples of Avicel and SEB, the bound dye reached within 5% of B_{max} at dye concentrations of 2 mg/mL. For DY11, the B_{max} was 22 mg/g and 28 mg/g for Avicel and SEB respectively. For DO15, the B_{max} was 25 mg/g and 29 mg/g.

For organic solvent pretreated samples, 3 mg/mL of DY11 were allowed to adsorb for 6 hours at 70˚C with moderate shaking. Free and bound dye values were obtained as described previously.

2.2.5 Enzymatic Hydrolysis

Cellulase from *Trichoderma reesei* (Celluclast®, 85 Filter paper units (FPU)/mL), β-glucosidase from almonds (5 U/mg) were purchased from Sigma-Aldrich. Cellic CTec2, a cellulase mixture was graciously provided by Novozymes (Franklinton, NC). Experiments were performed in 1 mL of 50 mM sodium acetate buffer (pH 5) with 2% (w/v) solid loading. Celluclast and Cellic CTec2 reactions were shaken at 45°C and 50˚C, respectively, for a specified time. Reaction conditions were advised by Novozymes and selected for highest activity (Novozymes A/S 2010). Celluclast, Cellic CTec2, and β-glucosidase loadings were 17.5 FPU/g substrate, 25.0 FPU/g substrate and 125 U/g substrate respectively. The reducing sugar content was measured by 3,5 dinitrosalicylic acid assay (Miller 1959). The free reducing sugar was compared with initial substrate to determine the hydrolysis yield.

2.2.6 Dynamic Light Scattering

Dye samples were filtered through 0.2 µm syringe filters from VWR International and subsequently diluted using reagent grade water from Sigma-Aldrich. These samples were measured for particle size distribution on a Malvern Zetasizer Nano (Malvern, UK).

2.3 Results and Discussion

2.3.1 Correlation between bound dye and cellulose hydrolysis

Pretreatment of lignocellulose with acid, base, or different organic solvents alters the accessibility of substrates to various extents. Thus, the treated substrates have a range of propensities towards cellulose hydrolysis by cellulase enzymes (Shuai and Luterbacher 2016). An effective probe should be able to track these changes. The correlation between the glucose yield and adsorbed DY11 dye in Figure 2 demonstrates the dye's effectiveness as a probe for several pretreated SEB samples. These SEB samples were meshed to a particle size of 75 µm to 150 µm (100 - 200 mesh), compositional analysis was performed (APPENDIX A.1), and the samples were treated with a variety of mild organic solvents. These effective pretreatments enabled high levels of glucose production in a short, 2-hour hydrolysis reaction. DY11's correlation compares favorably to that of DO15 and provides evidence that DY11 may be used as an alternative dye in modified Simons' Staining. Repeated experiments on individual solvents demonstrate consistent differences between high and low accessible pretreatments.

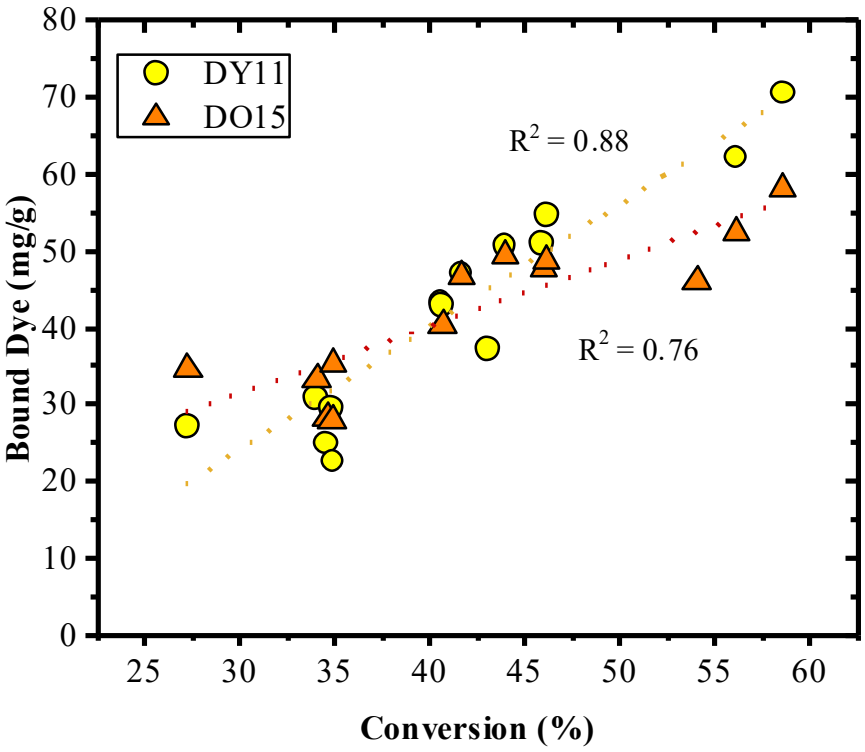


Figure 2. Adsorbed DY11 and glucose yields on pretreated SEB. Each data point represents a different organic solvent pretreatment.

To further examine this claim, experiments were performed comparing DY11 to DO15 for several model substrates, both cellulosic and lignocellulose. DO15 has been used in single probe assays with lignocellulose, and the results have yielded positive correlations between the maximum adsorption of dye and the enzymatic hydrolysis yields (Chandra and Saddler 2012).

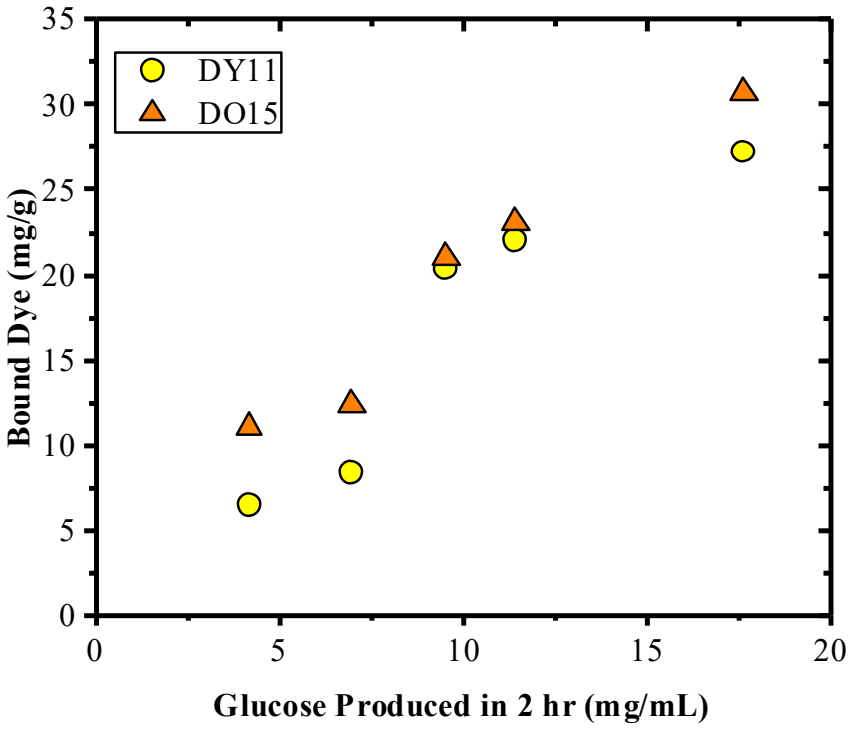


Figure 3. Adsorbed DY11 or DO15 and glucose yields on cellulose and lignocellulose substrates.

Figure 3 shows a comparison between DY11 and DO15 acting as single-dye probes tracking accessibility of SEB and SELP, Avicel, and two phosphoric acid treated samples (swollen cellulose and SEB).

Both dyes demonstrate similar bound dye values and accessibility trends with respect to glucose production. Additional experiments on treated and untreated fibrous cellulose provided similar results. For different batches of dye, similar trends are seen between substrates, but different absolute values of maximum adsorption are measured. This effect occurs with both DY11 and DO15, and extinction coefficients must be determined for each batch individually.

Efficacy in tracking increased glucose yield is not the only requirement for an alternative probe to DO15. Adsorption experiments with individual dyes on Organosolv lignin suggest that the direct dyes do not unproductively adsorb to lignin. Figure 4 highlights this adsorption and provides evidence that the bound dye measurements may be considered measures of accessible cellulose. Of note in Figure 4, both direct azo-stilbene dyes have less adsorption than 0.15 mg/g substrate, or two orders of magnitude less than the adsorption of dye on to cellulose. Additional experiments performed on EtOH-soluble lignin confirmed this finding.

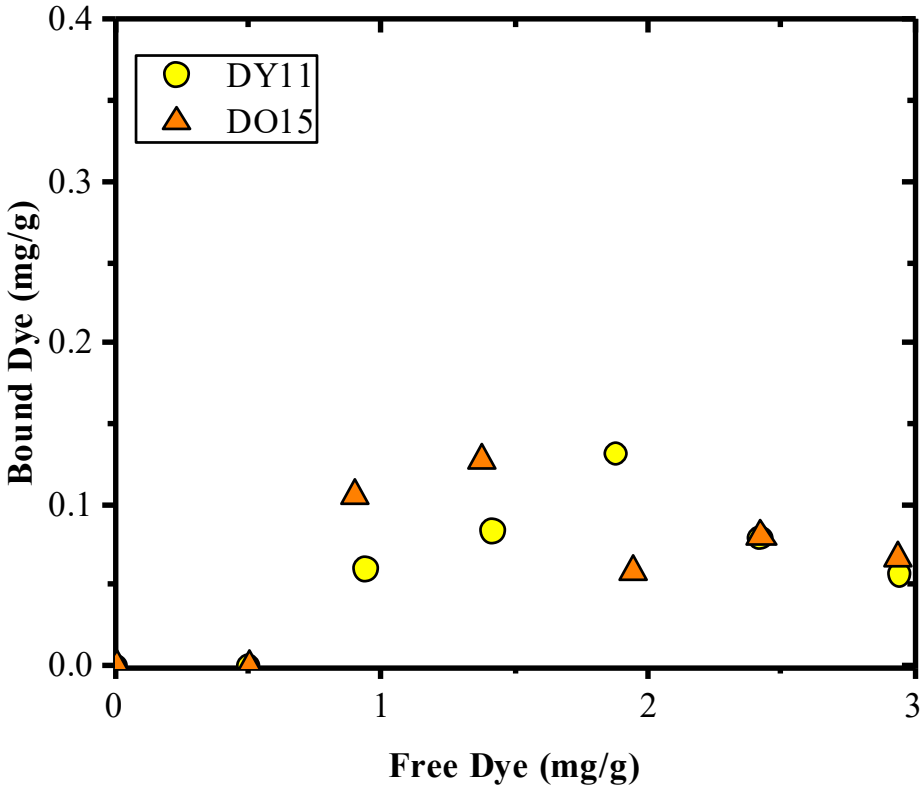


Figure 4. Adsorbed DY11 or DO15 on organosolv lignin after 6 hours at 70˚C with moderate shaking.

2.3.2 Size, ionic strength of DY11 and DO15

While tracking accessibility through a substrate's propensity towards glucose conversion is an essential characteristic of an effective probe, there are several additional factors that should be considered. Among them are size similarities to cellulase enzymes, the ease and stability of the assay, and the potential for measurements of both interior and exterior surface area.

In a 1995 study, Yu et al. determines the hydrodynamic size of HMW DO15 to be 5-36 nm (Yu, Minor et al. 1995). This size is similar to the published 6 nm size of cellulase enzyme complexes, and therefore lends merit to the hypothesis that all dyed fractions are accessible to cellulase enzymes (Yu, Minor et al. 1995, Chandra, Arantes et al. 2015). When comparing dynamic light scattering (DLS) results for DO15 and DY11 in Figure 5, it is clear that their respective HMW and LMW fractions are similar in size. More notably, the hydrodynamic size of DO15's HMW fraction is much larger than previously thought.

The DLS results in Figure 5 suggest that the average hydrodynamic diameter of the HMW fractions of both DO15 and DY11, retained behind a 100 kDa filter, is a full order of magnitude larger than the measured cellulase size of 6 nm. The measured hydrodynamic diameters had a range of values from 15 nm to 150 nm between various samples suggesting that the hydrodynamic size distribution plays a role in absolute bound dye variability.

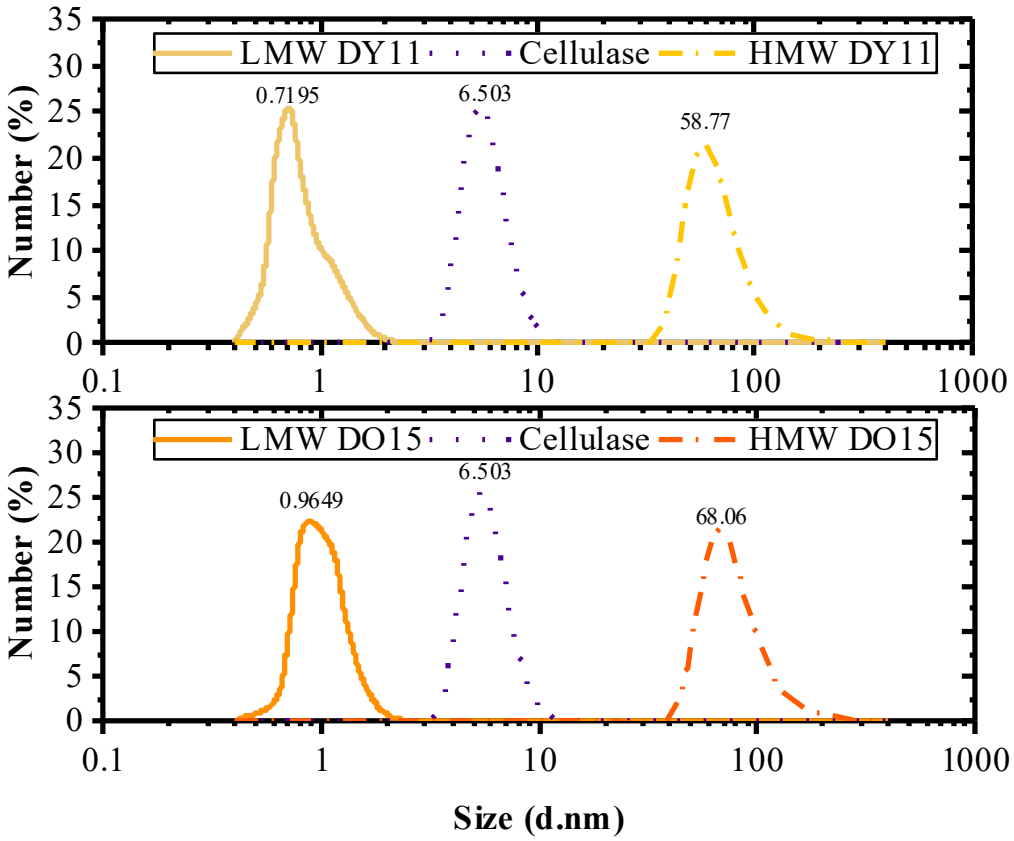


Figure 5. DLS results of (a) DY11 and (b) DO15 high/low molecular weight (HMW/LMW) fractions.

To further understand the constraints of using DY11 as an alternative probe for DO15, the aggregation and precipitation tendencies were analyzed. Table 2 shows a part of the pH and salt concentration studies that determined that the combined saline concentrations should remain below 50 mM in solution. Although increasing pH value enhanced absolute adsorption of DY11, we chose to perform the adsorption experiments in a pH 6 buffer with final concentrations of 30 mM sodium phosphate and 14 mM sodium chloride. This selection showed no relative differences between sample adsorptions and is more representative of the hydrolysis conditions at pH 5.

Table 2. Adsorbed DY11 on Avicel with various salt and pH buffers

DY11 [mg/g]	pH 4.0	pH 6.0	pH 8.0
0 mM NaCl	9.12 ± 0.48	9.02 ± 0.67	11.71 ± 1.54
5 mM NaCl	9.70 ± 0.67	10.46 ± 1.25	12.00 ± 1.34
14 mM NaCl	12.29 ± 1.34	12.38 ± 1.63	13.54 ± 1.44
50 mM NaCl	Aggregation	Aggregation	Aggregation

2.3.3 Potential for a standard Simons' Stain with DB1

The single-dye assay provides strong evidence for accessibility and supports the use of DY11 as an alternative dye for DO15. Additionally, a more traditional two-dye assay with DB1, can provide additional accessibility information and insight into organic solvent pretreatment effects (Yu, Minor et al. 1995, Inglesby and Zeronian 1996).

As seen in Figure 6, there is a difference between how the two azo-stilbene dyes behave when paired with DB1. In Figure 6b, interactions between DO15 and DB1 are demonstrated to the right of the isosbestic point at 554 nm. The sample with the most DO15 has the least absorbance at 600 nm.

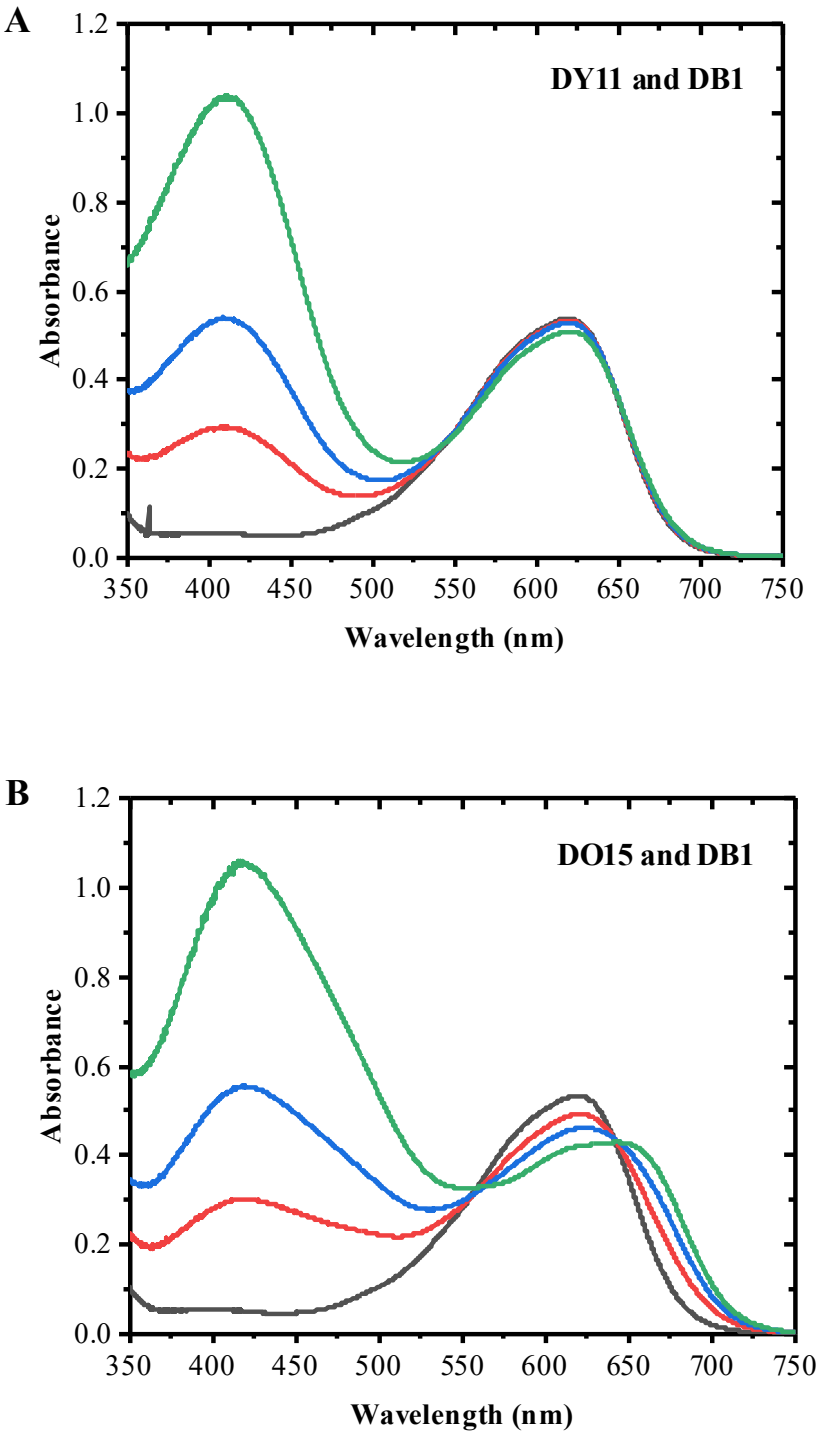


Figure 6. Absorption spectra of DB 1 mixed with four concentrations of (a) DY11 or (b) DO15.

To characterize these dual dye spectra, the Beer-Lambert law may be extended as

$$\begin{aligned} A_{412nm} &= \varepsilon_{O/412} L C_O + \varepsilon_{B/412} L C_B + \varepsilon_{OB/412} L C_O C_B \\ A_{620nm} &= \varepsilon_{O/620} L C_Y + \varepsilon_{B/620} L C_B + \varepsilon_{OB/620} L C_O C_B \\ A_{620nm} &= \varepsilon_{O/620} L C_Y + \varepsilon_{B/620} L C_B + \varepsilon_{OB/620} L C_O \end{aligned} \quad (1)$$

for DO15 and DB1, and as

$$\begin{aligned} A_{412nm} &= \varepsilon_{Y/412} L C_Y + \varepsilon_{B/412} L C_B \\ A_{620nm} &= \varepsilon_{Y/620} L C_Y + \varepsilon_{B/620} L C_B \end{aligned} \quad (2)$$

for DY11 and DB1.

In Equation 1 the extinction coefficients are modeled using a bilinear term containing the concentration of DO15 and DB1. However, a bilinear term is not required for the combination of DY11 and DB1 in Equation 2. The exact value of each of these extinction coefficients varies between batches, and standardization should be performed for each batch. The extinction coefficients for the results presented in Figure 6 are listed in Table 3.

Table 3. Extinction coefficients for each dye based on dye standards.

$\frac{mL}{mg \cdot cm}$	ε_O	ε_Y	ε_B	ε_{OB}
412 nm	55.4	52.2	6.6	0.09
620 nm	0.04	0.02	62.1	-4.9

While two dyes are not necessary for internal fiber accessibility measurements, the ability to easily determine individual dye concentrations in mixtures is important for comparing results between studies, and it may prove useful in future applications.

2.3.4 Correlating bagasse treatment to wood chip treatment

Expanding on the results presented in Figure 2, a total of 18 representative organic solvents were selected as a basis pretreatment group (APPENDIX A). These compounds were used to pretreat SEB samples. The resulting solids were assessed for accessibility, delignification capability, and glucose conversion. Figure 7 shows how the amount of bound dye, corresponding to accessibility, correlates much better with glucose conversion than the amount of delignification.

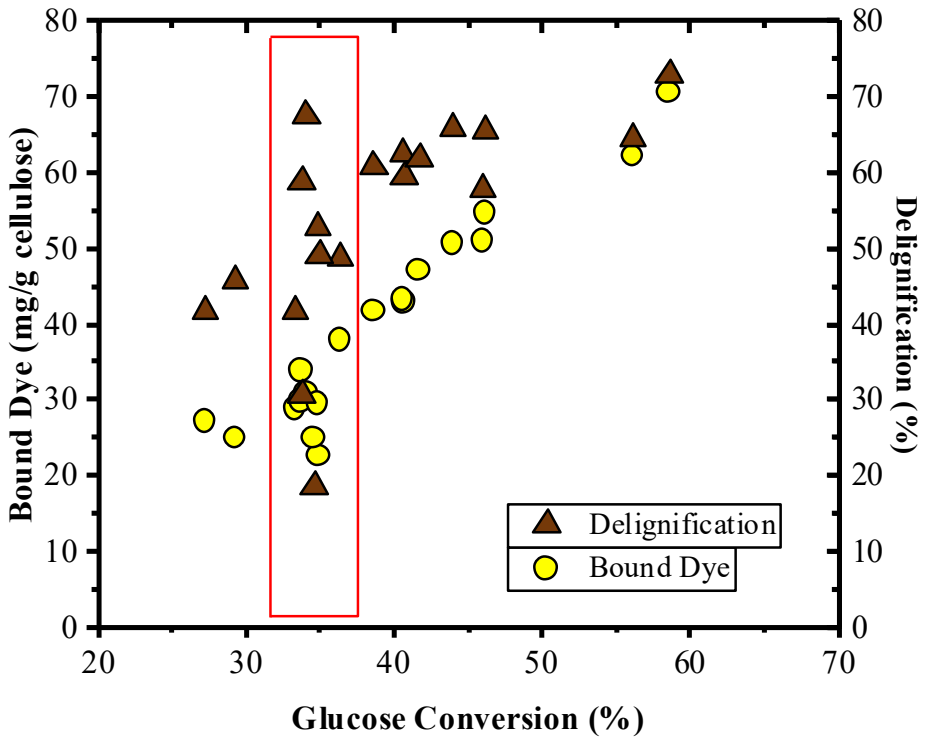


Figure 7. Delignification, accessibility, and conversion effects of chemical pretreatments.

Additionally, when plotted together, delignification and accessibility showed only minimal correlation to each other. This result confirms the hypothesis that there is a mechanism for cellulose swelling that is separate from the removal of lignin from the cell-wall matrix.

As highlighted by the red box in Figure 7, a cloud of 8 solvents show large variations in delignification with only slight variation in conversion and bound dye. This suggests that these compounds perform delignification in a way that does not alter the cellulose pore size distribution. An examination of the chemical structures of these solvents suggests that delignification is enhanced by more chalcogens (Group 16 atoms) in a heterocyclic solvent and with the addition of carbonyl groups to heterocycles.

Outside of the cloud of 8 solvents, this DY11 work highlights the high levels of delignification, accessibility, and conversion of heterocyclic solvents containing nitrogen. It is hypothesized that a free proton on nitrogen containing solvents is essential for high delignification and high conversion. This free proton supports the dissolution of lignin in the solvent. Interestingly, only half of the nitrogen containing heterocycles directly solubilized lignin in SEB. The other half altered the lignin to be highly soluble in a water-solvent mixture. A water wash after treatment extracted high levels of lignin from these SEB samples.

Towards implementing LVPP, we hypothesized that a correlation would be found between delignification of SEB and delignification of wood chips. A delignification study to compare treatments on two different biomass feedstocks is presented in Figure 8.

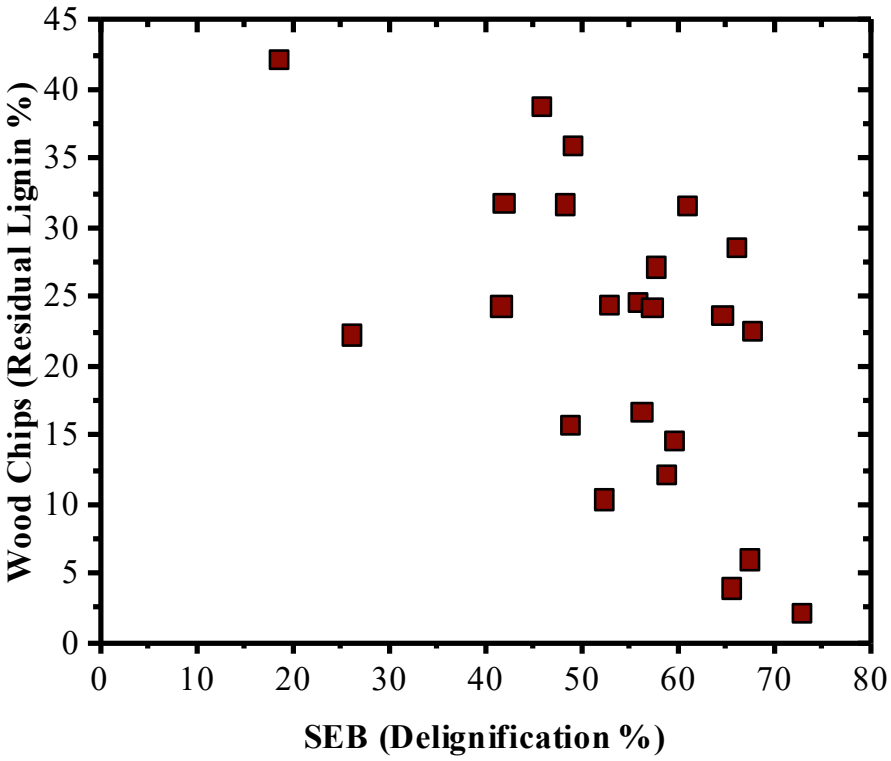


Figure 8. Comparison of residual lignin in wood chips and delignification of SEB.

We present evidence that the efficacy of organic solvent pretreatments is not transferable across feedstocks and that additional experimentation must be performed. The Spearman's rank correlation between delignification of SEB and residual lignin of wood chips after treatment is insignificant at -0.53. The process development and organic solvents utilized on agricultural residue may provide guidance, but an LVPP process that utilizes wood chips cannot rely on prior biofuels research to select the best organic solvent.

2.4 Conclusions

DY11 may replace DO15 as an alternative azo-stilbene dye for a modified Simons' staining assay. Our comparative experiments demonstrate that DY11 performs as well as DO15 in all tests, and significantly better in some. Specifically, DY11 has slightly higher correlation with two-hour lignocellulosic conversion, performs better in a combined DY11-DB1 assay, and is currently commercially available. Although Pylam Products no longer sells DO15, this original dye may be purchased commercially from new sources overseas. However, as a polymeric chemical from a new supplier, full characterization is required prior to implementation in Simons' staining. Therefore, DY11 is still preferred over DO15.

As a suitable accessibility assay, DY11 may be utilized to enhance our understanding of cellulose disruption kinetics and cellulase kinetic rate equations. Combined with delignification and initial hydrolysis rates, a simple calculation could enhance a cellulase kinetics model developed for pure cellulose (Bansal, Vowell et al. 2012). This model could then be extended to lignocellulosic substrates and evaluated if accessibility is a key determinant of enzymatic hydrolysis for lignocellulosics.

DY11 is a quick screen that correlates to the digestibility of treated screens. As LVPP expands, one could envision a future where some of the treated biomass is used for sugar production. Simons' staining, already available in the pulp industry, could then be utilized effectively on site. The present work on DY11 accessibility highlights the limitations of transferring research across feedstocks. The lack of correlation between DY11 adsorption, delignification of SEB, and delignification of wood chips exemplifies the need for additional research to select a solvent for LVPP. This will be discussed in CHAPTER 6.

CHAPTER 3. PREDICTING WOOD CHIP DELIGNIFICATION

3.1 Introduction

As discussed in CHAPTER 2, delignification efficacy in one feedstock does not necessitate efficacy in another. However, an effective screen to predict delignification of slash pine chips is key to exploring a large set of solvents for LVPP. Finding a solvent that selectively removes lignin is the first step in realizing the success of an LVPP process.

Lignin is a valuable commodity and a natural aromatic building-block for high-value products including low-cost carbon fiber, engineering plastics, thermoplastic elastomers, polymeric foams, membranes, and a variety of chemicals (Ragauskas, Beckham et al. 2014). Delignification of biomass removes the physical barrier around cellulose that restricts breakdown of cellulose to fuels and fiber bonding for paper applications. As new pathways from lignin to chemicals are discovered, the isolation of a lignin rich stream is increasingly important.

The prevailing strategy to isolate lignin from biomass is from the black liquor of a Kraft pulping system. Traditionally burned for energy, commercial technologies have emerged to extract lignin from black liquor using acids or carbon dioxide (Tomani 2010). A variety of ultrafiltration techniques have also been published (Wallberg, Jönsson et al. 2003, Kevlich, Shofner et al. 2017). Removing lignin from a pulp mill is economically attractive because it reduces the lignin load to the recovery boiler and creates a new revenue stream. However, lignin extraction after a high severity Kraft cook leads to a condensed lignin with a high sulfur load (Hu, Du et al. 2016). An alternative to Kraft lignin is the isolation of lignin by organic solvents. This organic solvent processing leads to a variety

of different lignin types, many of which retain a majority of native β-ether linkages (Holladay, White et al. 2007). There are many counter examples to this generalization, specifically with the addition of acids and high temperatures, and it is important to characterize the lignin produced in each organic solvent process (Rinaldi, Jastrzebski et al. 2016). However, without a robust understanding of both the delignification mechanism and the final form of lignin, the community has not developed predictive capabilities for delignification efficacy.

Methods of delignification all involve the cleavage of the linkages holding the various monolignols together (Gellerstedt and Lindfors 1984). In Kraft pulping, an aqueous alkali solution cleaves these linkages and produces phenolic hydroxyl groups that enhance lignin solubility (Chakar and Ragauskas 2004). In acidic systems, easily hydrolysable α-ether linkages are broken, and the β-aryl ether bonds are also broken under many conditions (McDonough 1992). All organic solvent pulping processes rely on chemical breakdown of lignin before it is dissolved, and typically the catalyst is an acid. Under certain conditions, the solvent or water may deacetylate the hemicellulose (Ferrini and Rinaldi 2014) and decrease the solution pH enough to autocatalyze the chemical breakdown of lignin (Santos, Hart et al. 2013).

The main functions of the organic solvent are to impregnate the plant tissue and solubilize the fragmented lignin fragments (Rinaldi, Jastrzebski et al. 2016). Solubilization of lignin has been explored and modeled on a variety of different lignin samples. Since the 1950s, studies have looked at the solubility of extracted lignin in hundreds of solvents and solvent mixtures (Schuerch 1952). Correlations have been established between lignin solubility in organic solvents and thermodynamic properties, such as the Hildebrand

parameter (Balogh, Curvelo et al. 1992) or Hansen Solubility (Hansen 2002), or linear free energy relationships, such as the Kamlet-Taft parameters (Parviainen, King et al. 2013). However, these correlations are able to explain the solubility of certain lignin types, but there is little empirical data exploring the connection between solubility and pretreatment of biomass. These thermodynamic studies are frequently referenced to both predict lignin solubilization in organic solvents and to increase delignification of biomass (Quesada-Medina, López-Cremades et al. 2010, Ye, Liu et al. 2014).

This work focuses on solvent-water mixtures with no acid or alkali catalysts. Despite this constraint, biomass pretreatments may be performed at a variety of different temperatures (140˚C – 220˚C), cooking durations (30 min – 6 hours), liquor-to-wood ratios (4:1 – 10:1), solvent loadings (0% – 100%), and chip sizes (sawdust to chips). With so many variables, it is difficult to compare solvents comprehensively. Herein, we explore one pretreatment strategy that was optimized for the greatest delignification separation on juvenile slash pine chip screened between 4 mm and 8 mm roll-screens. Using a moderately severe treatment, we are able to rank-order solvents based on their delignification efficacy and selectivity. The solubility part of the study utilizes a standard source of industrial lignin, namely ethanol extracted lignin, which can be easily obtained or produced internally. This study explores the use of a simple solubility experiment to screen solvents for LVPP, and it explores the relationship between this lignin solubility and slash pine delignification. Herein, we present correlation data between an organic solvent's ability to solubilize ethanol extracted lignin and its ability to delignify slash pine chips. We utilize this data for rank-ordering a subset of solvents for LVPP.

3.2 Materials and Methods

3.2.1 Substrates

Lignin samples were donated by American Process Inc. (Thomaston, GA). Mixed hardwood was treated with a mixture of sulfur dioxide, ethanol, and water at 150˚C. The resulting liquor was distilled to remove ethanol and sulfur dioxide which resulted in lignin precipitation. The precipitate was separated by centrifugation and water washed. For all solubility experiments, the lignin was sieved to a size fraction of 75 µm – 150 µm and oven dried at 50˚C. For characterization experiments, the lignin was sieved to a size fraction of 300 µm to 200 µm. Juvenile slash pine woodchips were provided by Georgia Pacific (Memphis, TN) from a source in (Foley, FL). All woodchips used in experiments were screened through 4-8 mm roll screens. The organic solvents used, ethanol (EtOH), 1-MI, ethylene glycol (EG), THF, and 1,6 hexamethylenediamine (HMDA), were purchased from VWR International (Radnor, PA).

3.2.2 Solubility

300 mg of lignin were weighed into 50 mL centrifuge vials. 10 mL of organic solvent/water mixture were added, and the solution was mixed for 4.5 hours on a rotating mixer at 23 ˚C. The undissolved lignin was recovered by vacuum filtering the solution through Whatman 934-AH glass microfiber filters in oven dried crucibles. The crucibles were oven dried at 50˚C for 2 days and then weighed to determine the mass of undissolved lignin. The solubility factor (Simitzis, Sfyrakis et al. 1995) was calculated as Equation 3:

$$Solubility\ Factor = \frac{mg\ lignin\ recovered}{mg\ lignin\ originally\ added}. \quad (3)$$

3.2.3 Treatment

Woodchips were air dried in a fume hood for 2 days, reducing their moisture content to ~7%. 6 g of woodchips and 60 mL of organic solvent/water mixture were added to a 600 mL Parr benchtop reactor with temperature control. The solution was treated at 200˚C for two hours, not including a 20-30-minute warmup time. The resulting mixture was screened to recover the woodchips, which were subsequently washed in excess water for 18 hours. The washed woodchips were re-weighed after drying in a fume hood for 2 days. The order of the treatments was randomized before starting.

3.2.4 Delignification

Klason lignin was determined as described in 2.2.3. In short, a modified version of NREL's Determination of Structural Carbohydrates and Lignin in Biomass is employed on milled samples. Each sample was treated with sulfuric acid and then filtered to collect the remaining solids.

3.2.5 Gel Permeation Chromatography (GPC)

The weight-average and number-average molecular weights of the EtOH-extracted lignin was determined on two PL-gel 10 mm Mixed-B 7.5 mm i.d. columns. 5 mg samples were dissolved in 2 mL of tetrahydrofuran and passed through a 0.2 μm syringe filter. A 15 μL sample was injected and the column was operated at 30˚C with stabilized THF as the mobile phase at a flow rate of 1.0 mL/min. Monodisperse polystyrene was used as the standard for molecular weight calculations.

3.2.6 2D Heteronuclear single quantum coherence spectroscopy (2D-HSQC-NMR)

2D-HSQC-NMR spectra were recorded on a Bruker AVIII 400 MHz spectrometer at 25˚C in dimethyl sulfoxide (DMSO)-d6. Lignin in DMSO-d6 at a concentration of ~100 mg/mL was measured with spectral widths of 5000 Hz and 20000 Hz for the 1H and 13C dimensions, respectively. The number of collected complex points was 1024 for the 1H dimension with a recycle delay of 1.5 s. The number of transients was 64, and 256 individual time increments were recorded in the 13C dimension. The 1 JCH used was 145 Hz. Prior to Fourier transformation, the data matrices were zero filled to 1024 points in the 13C dimension. Data processing was performed using standard Bruker Topspin-NMR software. The central solvent (DMSO) peak was used as an internal chemical shift reference point (δC/δH 39.5/2.49).

3.2.7 Attenuated Total Reflection Infrared Spectroscopy (ATR-IR)

Samples were ground and sieved to a particle size of 40-80 mesh and placed into a vacuum desiccator at room temperature overnight to dry. The dry lignin was analyzed using a Thermo Scientific Nicolet 8700 infrared spectrometer equipped with a Smart iTR (ZnSe crystal) sample port and an MCT detector. Spectra were taken at 4 cm^{-1} resolution and averaged over sixty-four individual scans.

3.3 Results and Discussion

3.3.1 Characterization of Technical Lignin Sample

Towards a viable screen for LVPP solvents, we selected and characterized a technical lignin sample, as seen in Figure 9. In Figure 9A we distinctly observe the S aromatic signals ($S_{2/6}$) along with the G aromatic signals (G_2, G_5, and G_6). In Figure 9B we

observe the prevalence of methoxyl, β-O-4 and β-β linkages. In Figure 9C we see the ATR-IR profile with strong aromatic and C-O stretching. In Figure 9D, the molecular weight profile is mapped to demonstrate an average molecular weight of 1080 g/mol. Together, this lignin characterization shows a typical hardwood lignin that has been partially delignified but still contains similar linkages to native lignin. This lignin is reproducibly available and an industry standard for technical lignin. Full characterization is presented in APPENDIX B.

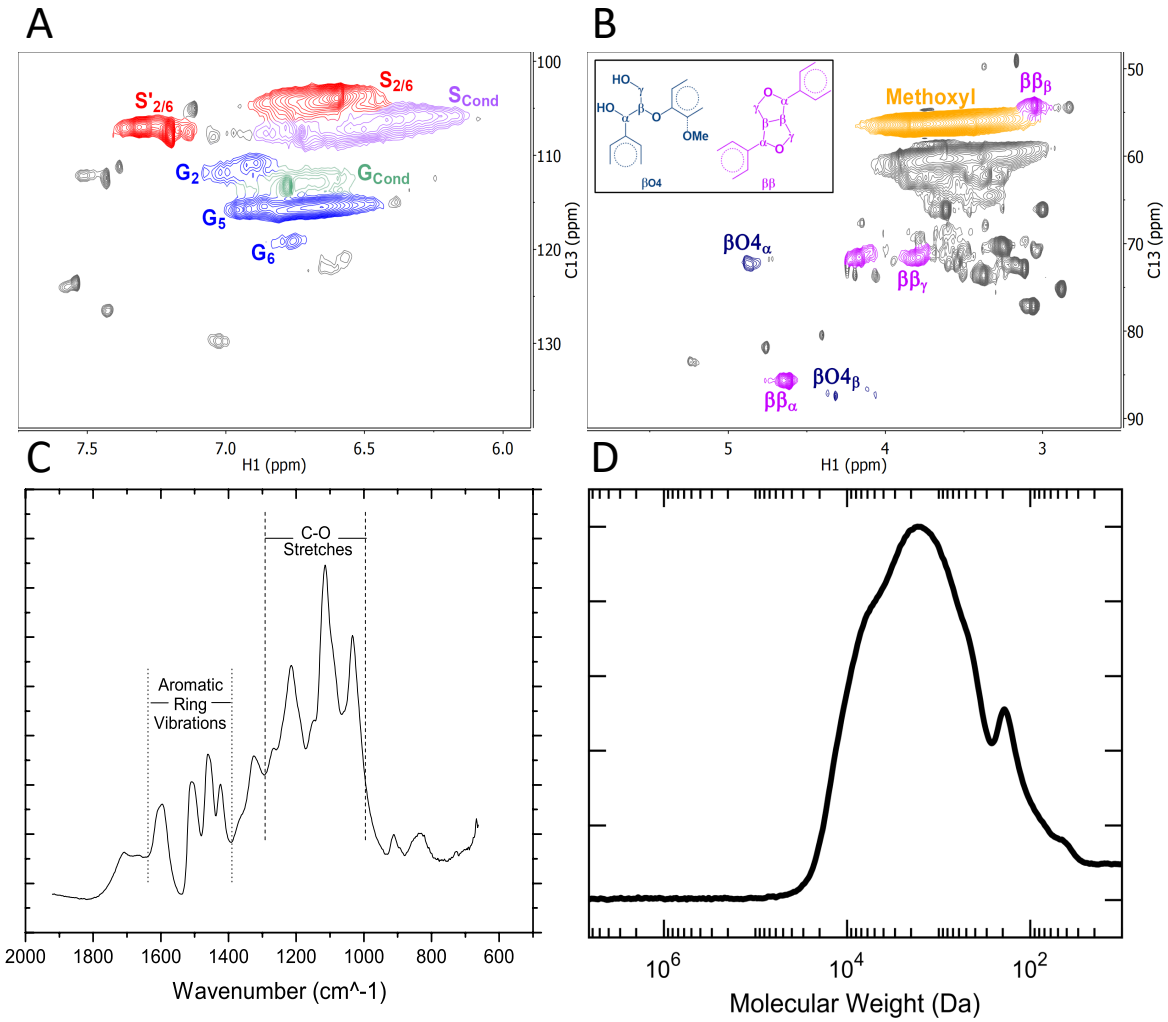


Figure 9. Ethanol extracted lignin, characterized by 2D-HSQC-NMR (A and B), ATR- IR(C), and GPC (D).

3.3.2 Solubility of technical lignin in five organic solvents

Towards determining a relationship between technical lignin solubility and woodchip delignification, we explored five organic solvents (EtOH, 1-MI, EG, THF, and HMDA) at five different organic solvent fractions (0.1, 0.3, 0.5, 0.7, and 0.9) in water. The lignin solubility fraction of each aqueous solvent mixture is depicted in Figure 10.

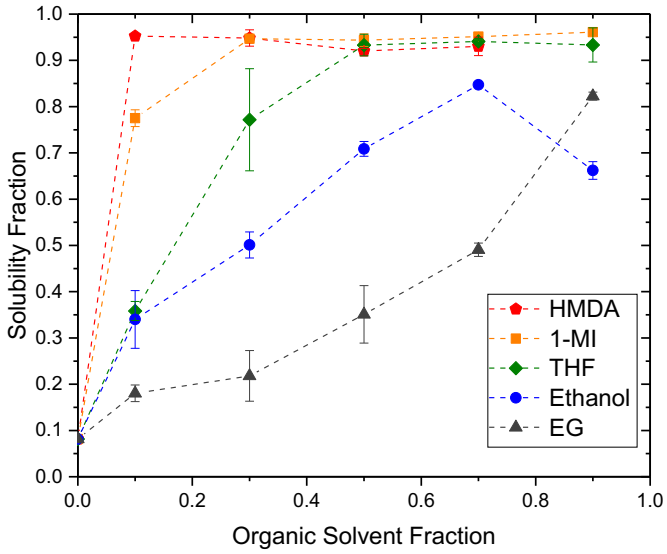


Figure 10. Room temperature lignin solubility fractions of five organic solvents at varying organic solvent fractions. Error bars indicate the standard deviation. Lines connecting the data points are visual aids and do not indicate measured data.

We note that HMDA and 1-MI solubilize the greatest fraction of lignin across the five organic solvent fractions, followed by THF, EtOH, and EG. Each solvent demonstrates a unique lignin solubility profile, but several patterns emerge. The solubility fraction of all solvent mixtures drops as the organic solvent fraction approaches zero. EG is the only solvent to have a solubility fraction below 0.9 at an organic solvent fraction of 0.7, and it is the only solvent where the solubility continues to increase at higher solubility fractions. The difference of solubility fractions between the solvents is greatest at 0.1 and 0.3 solvent

fractions. The solubility for EtOH mixtures exhibits the shape pattern reported in literature (Ni and Hu, 1995). The large difference in solubility at 0.3 solvent fraction provides a straightforward choice for rank-ordering of organic solvents.

3.3.3 Solubility is not a predictor of delignification of slash pine chips

This rank-ordering of organic solvents does not correlate with the trends of slash pine delignification after treatment at 200˚C for two hours (Figure 11).

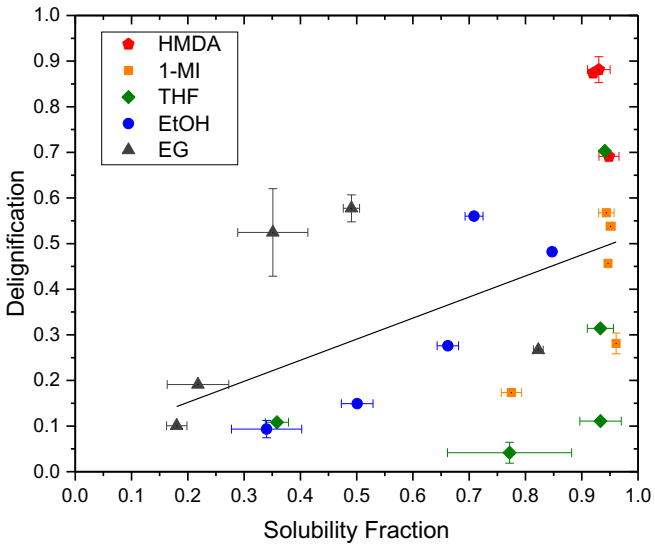


Figure 11. Comparison between 25˚C lignin solubility fraction and woodchip treatment delignification (200 ˚C, 2 hrs). Error bars indicate the standard deviation. Lines connecting the data points are visual aids and do not indicate measured data.

The residual lignin content and delignification of wood chips are compared to the technical lignin solubility, and Figure 11 shows a wide range of delignification efficacy (11% - 88%) at solubility fractions above 0.8. There is a smaller range of delignification efficacy (0% - 28%) below 0.8 solubility for all solvents except EG. The simplest glycol, and a solvent used in pulping of alternative feedstocks (Jiménez, Perez et al. 2008), EG is

an outlier and confirms that low solubility cannot screen out organic solvents without risking the loss of a promising solvent. From this data, we note that lignin solubility in organic solvent mixtures cannot predict delignification efficacy of pine wood chips

3.3.4 Impact of water concentration on delignification of pine chips

Another finding from this work is the requirement of at least 0.1 volume fraction of both solvent and water. Figure 12 shows that for both low (0.1) and high (0.9) organic solvent fractions, the delignification is low regardless of the solubility.

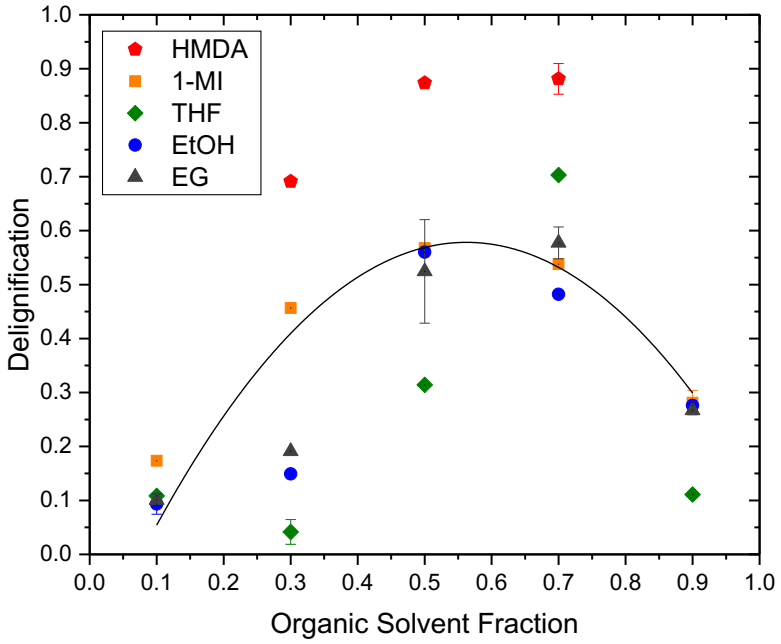


Figure 12. Comparison between the organic solvent fraction and the woodchip treatment delignification (200 ˚C, 2 hrs) with fitted 2nd order polynomial. Error bars indicate the standard deviation. Lines connecting the data points are visual aids and do not indicate measured data.

At high solvent fractions > 0.9, rate and extent of delignification likely suffer from a shortage of water which catalyzes lignin depolymerization reactions (Rinaldi, Jastrzebski

et al. 2016). This feature partly explains the wide range of delignification percentages at high solubility fractions. Figure 12 also shows that there exists a maximum delignification achieved by each of the organic solvent mixtures with water. The EtOH maximum delignification at 0.5 organic solvent fraction matches published acid-free Organosolv results (Yáñez-S, Matsuhiro et al. 2014). Similarly, the EG maximum delignification at 0.7 organic solvent fraction is close to the 0.8 fraction used for alternative feedstock pulping (Alriols, Tejado et al. 2009). This finding suggests that the primary organic solvent fraction range of interest for LVPP is between 0.5 and 0.7. As 0.5 allows for a lower solvent purity compared to a 0.7 pretreatment, we propose the use of a 0.5 screen for LVPP due to economic constraints on separations.

Given an incoming biomass stream at 50% solids and a 4:1 L/W ratio, a treatment stream at 0.67 solvent purity is required for a final solvent concentration of 0.5. In contrast, to obtain a final solvent concentration of 0.7, the treatment stream would require a 0.93 solvent purity. Additionally, a wood chip moisture content increase to 55% would include too much water to reach a 0.7 final solvent treatment regardless of solvent purity. For high-boiling solvents, the economic benefits of removing less water are significant (Chrisandina, Kwok et al. 2019).

At 200˚C and 2 hours, our pretreatment severity provides a wide range of delignification efficacy and is more severe than standard Kraft cooks. Any greater severity would be impractical within an LVPP framework. Another finding of note is the connection between high solubility and a wider range of organic solvent fractions that can effectively delignify wood chips. Solvents such as HMDA and 1-MI with broad solubility profiles

have small decreases in delignification between 0.7 and 0.3 solubility fractions. This finding could be explored with a larger set of solvents.

To quantify the predictive power of solubility and organic solvent fraction for delignification efficacy, we fit a multilinear regression model from Figure 11 and Figure 12. The R^2 value of this model was 0.55 and a separate Spearman's rank correlation coefficient between the mixture solubility and delignification ranks was 0.49, which corresponds to a p-value of 0.32. These results show that there is a weak positive correlation but no predictive power. Whereas solubility would predict 1-MI to have the highest delignification and EG to have the lowest, we clearly see that delignification measurements are required.

While the room temperature solubility fraction of a solvent mixture to predict the extent of delignification is of limited use, this study highlights five solvents for LVPP and provides delignification data for aqueous solvent mixtures on pine chips. Quick solubility measurements may provide a guess of delignification efficacy and hint at the diminished efficacy of the solvent at lower solvent fractions. However, wood chip treatments at 50% - 70% aqueous organic solvent mixtures are required to rank order solvents for LVPP. The higher the delignification at severe conditions, the lower the LVPP pretreatment conditions required for partial delignification of wood chips prior to pulping. If the treatment does not yield a delignification of >60% at these severe conditions, the solvent should be precluded from future studies. The best solvents will delignify >80% at 200˚C and 2 hours, and the organic solvents may be ranked into quartiles based on removal of lignin from pine chips. Together, this pretreatment and quick solubility measurement enables the efficient determination of a solvent's capacity to delignify wood chips for downstream applications.

3.4 Conclusions

In this work, we evaluate delignification efficacy for organic solvents towards LVPP process development. We conclude that solubility of ethanol-extracted lignin in an aqueous-organic solvent mixture cannot predict the extent of delignification of slash pine chips. Nevertheless, the results provide insight into aqueous-organic solvent mixture delignification tendencies and provide the information required for a solvent screening parameter for LVPP. For a process that seeks to maximize solvent recovery, a pretreatment screen with 50:50 organic solvent:water is appropriate for LVPP. Alternative assessments may also utilize this data as a screening criterion to reject certain solvents with low solubilities at 30:70 organic solvent:water. While these screens may exclude a few key organic solvents, the benefits to a streamlined experimental process will enable a systematic approach towards designing a biorefinery compatible with pulp production.

This work is foundational to the performance criteria presented in CHAPTER 6. By exposing the requirement for high concentrations of both solvent and water, a single condition may be utilized in initial screening. Likewise, in presenting solubility profiles, this work highlights the variation of lignin solubility in low organic solvent loadings. While a high solubility fraction does not directly correlate to pretreatment efficacy, it is indicative of a broad range of solvent efficacy. Succinctly, if a solvent has a high solubility fraction at a 0.30 solvent loading, it will maintain its high solvent loading efficacy at lower solvent loadings. Low solubility solvents, such as EG, demonstrate precipitous decreases in delignification at lower organic solvent loadings. By contrast, high solubility fractions, such as 1-MI and HMDA, have smaller decreases. This trend continues across a larger set of solvents tested in CHAPTER 6.

CHAPTER 4. PROCESS DESIGN AND ECONOMICS FOR LVPP

4.1 Introduction

As discussed in CHAPTER 1, the Kraft pulping process consists of impregnating wood chips with steam, cooking them in a pressurized digester, blowing them into a collection tank, screening the fibers by a combination of sieves and centrifuges, washing those fibers in rotary drums, and finally bleaching them in vessels. The chemicals used to cook the chips are recycled by a series of evaporators, a recovery boiler and a lime kiln. This chemical recycling is essential for an economic process and a main focus of all mills.

While there may be future opportunities to fully utilize the Kraft mill in a one-step process with organic solvents, the two-step LVPP process requires the installation, or re-purposing, of several unit operations to economically produce a high-quality lignin stream (Kwok, Luettgen et al. 2017). Aside from an effective fractionation of biomass, the main driver of this process is the recovery of treatment chemicals. This recovery is enabled through the washing of solids, the separation of lignin, and the recovery of solvent. Figure 13 presents a schematic of a proposed LVPP process with five additional process steps, (1) a treatment in a Kamyr digester, (2) chip washing that acts as a feed to a pulp mill digester, (3) a lignin precipitation by CO_2, (4) a washing of solids in rotary washers, and (5) a distillation of an aqueous organic solvent mixture. Combined, these process steps enable LVPP to leverage the selective delignification of organic solvents with the effective pulp production of the Kraft process (Kwok, Luettgen et al. 2017). A higher quality lignin stream may be produced than alternative lignin production technologies, and the associated

revenue may be evaluated against LVPP's operating and capital costs. Each process step is considered in a techno-economic analysis for LVPP with HMDA as the solvent.

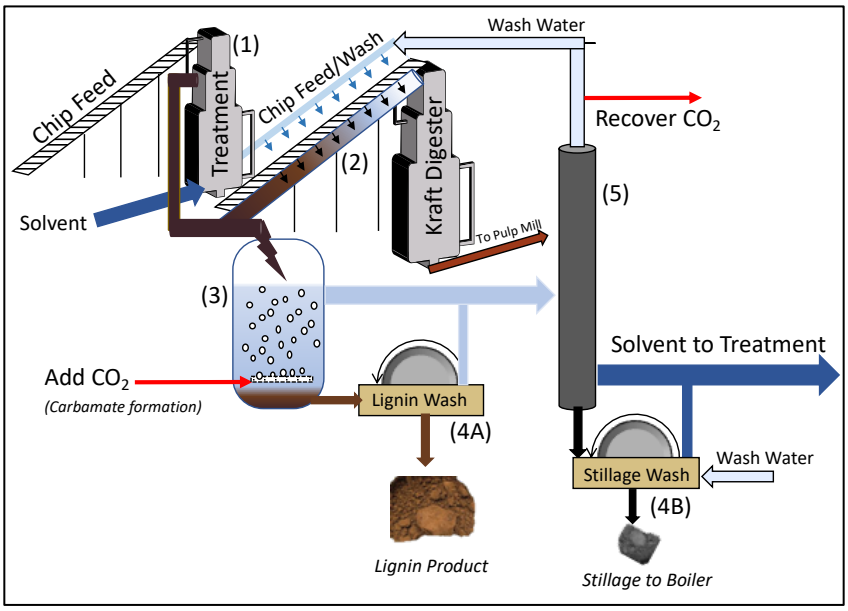


Figure 13. Schematic of LVPP process with 5 additional process units to add to a pulp mill.

4.2 Kraft Pulp Mills and LVPP analogues

4.2.1 Treatment of Wood Chips

The LVPP process hinges on an effective pretreatment step that selectively isolates lignin from wood chips. These pretreatments require elevated temperatures and equipment that can process a thousand tons of wood chips per day. Depending on the scale and implementation of LVPP, either batch or continuous digesters may be utilized. This work utilizes costing for continuous digesters that are most prevalent in the industry. Johan Richter's innovation of a continuous digester, or Kamyr digester, that flows wood chips and chemicals counter-current to each other is still utilized today (Richter 1949). Modern digesters can process upwards of 2000 dry tons of wood chips and have steaming zones

(Richter and Richter 1965), treatment zones, and washing zones (Laakso 1969). Initial steaming of chips allows the use of low-pressure steam for heat-up and removes air for improved impregnation (Svensson 1936, Gullichsen and Fogelholm 1999). The flowrates and temperature through the treatment zone are based on the understanding of biomass fractionation by the white liquor. Finally, the washing zone in the digester allows effective diffusion and displacement to reduce the load on downstream washing (Santos and Hart 2014).

LVPP will benefit from all three zones and the treatment stage will resemble a modern continuous digester. Reduced air and utilization of flash steam will aid the treatment effectivity and operating costs. An understanding of organic solvent fractionation will provide guidance for the necessary residence time in the digester. Finally, the washing zone will be a key factor in economic viability with improved solvent recovery. In this work, capital costs are assumed equal to that of a standard pulp mill digester. Increasing the reactor temperature is considered the main operating cost and is broken into two sections, one requiring low pressure steam (LP steam), and one requiring medium pressure steam (MP steam). Biomass fractionation is based on experimental data.

4.2.2 Washing of Wood Chips

Biomass washing in a typical Kraft mill takes two forms. There is an initial chip washing process at the front-end of the mill and rotary brownstock washing at the back-end. The initial chip washing process, pioneered by Valmet, cleans the outside of the chips to remove metal, dirt, and sand. The brownstock washing utilizes diffusion and displacement to remove the black liquor from the fibers. This is typically performed in rotary drums where the fibers form a mat on the rotating wheel with a shower on top and

vacuum pulling through the middle (Santos and Hart 2014). To remove treatment liquor from wood chips, a combination of these two techniques must be employed. Without modification, rotary drums that rely on fiber mats are not adequate for wood chips. An alternative washing process is proposed to combine vacuum washing with a feed to the digester (Figure 13). Capital costs are based on digester feed costs with added modification costs. Operating costs are based on water usage and solvent displacement assumptions.

4.2.3 Lignin Precipitation

There are multiple methods for precipitating lignin. Liquid-liquid extraction, anti-solvent precipitation, and water precipitation. Lignin recovery by water dilution has been proposed in several recent publications (Ligero, Villaverde et al. 2008, Chen, Dou et al. 2017) however the water requirement will be an insurmountable roadblock for full implementation in a pulp mill (Chrisandina, Kwok et al. 2019). Liquid-liquid extraction has been demonstrated to separate lignin from 2-methyltetrahydrofuran (Stiefel, Di Marino et al. 2017), but it is highly solvent dependent and adequate extraction solvents have not been determined for top LVPP solvents. Anti-solvents are frequently used in industry, and CO_2 is effective in industrial Kraft lignin precipitation (Tomani 2010). Consumption of CO_2 is assumed equal to that of LignoBoost, and the capital costs are assumed based on material costs (Tomani, Axegård et al. 2011). In this work, we select an amine solvent that forms a reversible carbamate with CO_2. HMDA has been explored as a CO_2 capture solvent (Mondal, Bandyopadhyay et al. 2017) and the CO_2 capture is reversible at slightly elevated temperatures. The carbamate formation produces free protons that can precipitate lignin and is a promising solution to lignin precipitation from organic solvent.

4.2.4 Solvent Recovery

Following separation of lignin from the solvent, solvent recovery from water is critical for an economic process. Three industrial separation techniques are distillation, reverse osmosis, and multi-effect evaporation. While the use of multi-effect evaporators is well established in the pulp industry as a water removal strategy, a side-by-side comparison of these three techniques suggests that adequate organic solvent recovery is only available through distillation (Chrisandina, Kwok et al. 2019). Thus, solvent recovery in LVPP will utilize distillation columns, along with their well-defined models, to calculate capital and energy costs associated with the separation. A key factor in this distillation scheme is the recovery of dissolved and suspended solids remaining in the mixture. In bio-ethanol production, several methods are used to treat the dissolved solids, termed stillage, that accumulate in the distillation column (Sajbrt, Rosol et al. 2010). This works dries the dissolved solids and recovers the solvent before sending the solids to the recovery boiler for energy recovery. Capital and operating costs are based on distillation columns modeled in ASPEN+. Additional details will be presented in CHAPTER 5.

4.2.5 Techno-economic analysis

After sketching a process design, modeling the economics of a system is required for evaluation. Techno-economic analyses evaluate each process decision and guide research and development. Biorefinery techno-economics have shown viable paths to market (Humbird, Davis et al. 2011), but they have also exposed high sensitivity to solvent recovery (Baral and Shah 2016) and biomass utilization (Joly and Verdade 2015). This work highlights key assumptions and areas for extended research. This work also describes the mass-flows to each unit and uses sensitivity analyses to show key economic drivers.

4.3 Results & Discussion

4.3.1 Assumptions made for mass balances

To complete mass balances for the process, certain assumptions are made for each unit operation and presented in Table 4.

Table 4. Most impactful assumptions for process flowsheet.

Unit Operation	Assumption	Reference
Feed	Feed is 125,000 kg/hr (Dry basis)	(Smook 1992)
Feed	Feed is 50% solids	Experimental
Feed	Feed is 33% lignin	Experimental
Treatment	Residence time = Pulp Mill digester RT	(Sävelin 2014)
Treatment	Lignin Removal Rate = 48.4%	Experimental
Treatment	Cellulose/Hemi Removal = 6.3% / 21.6%	Experimental
Treatment	Solvent Loading = 50%	Experimental
Treatment	Outlet Consistency = 31%	(Kautto, Realff et al. 2013)
Treatment	Solvent Cost = 0.648 $/kg	SECTION 6.3.3
Treatment	LP/MP Steam = $6.6/$10.5 per 1000 kg	(Seider, Seader et al. 2009)
Treatment	L/W Ratio = 4	(Smook 1992)
Chip Wash	Dilution Factor = 4.5	(Santos and Hart 2014)
Chip Wash	Overall Displacement Ratio = 0.98	(Kwok, Luettgen et al. 2017)
Precipitation	CO_2 Loading = 0.200 kg/kg lignin	(Tomani, Axegård et al. 2011)
Precipitation	Lignin Precipitation = 92%	(Tomani, Axegård et al. 2011)
Distillation	Stillage Wash Recovery = 0.95	(Henderson and Hjort 2016)
Distillation	Solvent Purity = 99.5%	(Chrisandina, Kwok et al. 2019)
Distillation	CO_2 Release = 100% (No HMDA loss)	(Strazisar, Anderson et al. 2001)
Distillation	Utility Cost = $4513 / hr	Estimates and ASPEN+
Solids Washing	Solids Washing = 2 kg/kg solids	(Tomani, Axegård et al. 2011)
Economics	Maintenance Costs = 15% of Capital	(Turton, Bailie et al. 2008)
Economics	Tax Rate = 25%	(Smook 1992)
Economics	IRR = 25%	Experimental
Economics	Operating Days = 350	Experimental
Economics	Overall Capital Cost = $84.3 MM	Estimates and ASPEN+
Pulp Mill	Increased Value of Wood Chips = 0%	Experimental

Given these assumptions, the inputs and outputs of the system are presented in Table 5 and the minimum lignin selling price is $829/metric ton.

Table 5. Inputs and outputs for LVPP process.

Inputs		
Type	Value	Units
Woodchips (Dry Basis)	125,000	kg/hr
Solvent (Pure)	3,499	kg/hr
Water (Pure)	164,666	kg/hr
CO_2	3,939	kg/hr
Outputs		
Type	Value	Units
Woodchips (Dry Basis)	94,300	kg/hr
Lignin	18,120	kg/hr
Solids to Burn	12,163	kg/hr

Feed assumptions are based on a 1500 ton/day pulp mill with juvenile slash pine chips that have a measured lignin content of 33% and a typical moisture content of 50%. Changes to the lignin content lead to significant changes in lignin selling price, assuming similar treatment efficacies.

Treatment assumptions are based on experimental results. Lignin, cellulose, and hemicellulose removal rates were measured for a 185˚C pretreatment and found to be 48.4%, 6.3%, and 21.6% respectively. For a typical Kraft pulp, the lignin, cellulose, and hemicellulose removal rates are approximately 90%, 48%, and 11% respectively (Fardim and Durán 2004). The cellulose and hemicellulose removal rates will impact the downstream value of the wood chips. Assuming a direct correlation between sugar removal and value of product wood chips, the sugar removal rates and lignin removal rate lead to

significant impacts on the lignin selling price. Other treatment assumptions do not yield significant changes to the lignin selling price.

Solvent recovery from the wood chips is the single-most important assumption and warrants further research. Current washing assumptions are based on brown-stock washing efficacy. These assumptions are most likely to over-estimate the amount of solvent recovered due to the mass transfer limitations of a wood chip compared to fibrous material. A 10% decrease in washing efficacy leads to a 38% increase in minimum lignin selling price. In contrast, the dilution factor, or amount of water added has minimal effect on the required lignin selling price.

Lignin precipitation has a direct impact on the quantity of lignin produced. Current assumptions are based on acid precipitation results across a variety of different solvents (Tomani, Axegård et al. 2011). The lignin selling price is significantly impacted by both the fraction of dissolved lignin that is precipitated and the reversibility of the solvent-carbamate reaction. Kinetic models have been established for CO_2 capture in diamines, but further experimentation is required to fully quantify the solvent recovery following lignin precipitation.

4.3.2 Economic Drivers for Techno-economic Analysis

A sensitivity analysis highlights the critical assumptions and their impact on the minimum lignin selling price. By changing the assumptions by 10%, or less if a limit is reached (denoted by a *), Figure 14 shows the impact on lignin selling price.

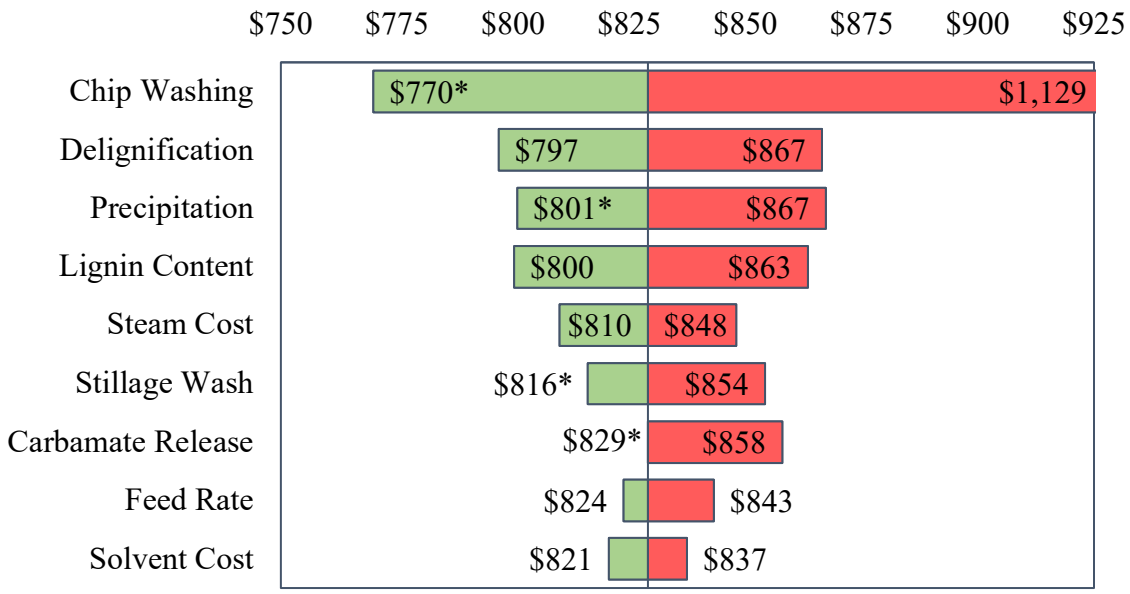


Figure 14. Most impacted lignin selling prices after 10% changes to assumptions.

Far and away the biggest driver of cost is the chip washing assumption of 0.98 overall displacement. Reducing this displacement by 10% leads to a 34% increase in lignin selling price. This increase would be exacerbated with changes to other assumptions, and it is a key process consideration. Together, this sensitivity analysis paints a picture of three key processes: (1) solids washing, (2) lignin precipitation (3) and carbamate regeneration. The common theme in each consideration is the recovery of solvent. Dilute solvent streams are lost throughout the system, and the challenges with recovering dilute streams will be addressed in CHAPTER 5.

In addition to this sensitivity analysis, a summary of the process costs was performed to better understand the key economic drivers. In total, the estimated installed capital costs are $84.3 MM, the operating costs are estimated at $71.5 MM/year, and the lost energy value due to product formation is estimated at $12 MM/year. Of the operating costs, approximately $19 MM/year are due to solvent losses and another $5.5 MM/year are

added due to the amount of water required. The biggest operating cost is the $38 MM/year steam requirement for distillation separation of HMDA and water and second largest cost is the $10 MM/year steam requirement to heat the treatment reactor. The calculations and assumptions for this scenario are detailed in the following section.

4.4 LVPP Process Flow Scenario

Based on the process sketched in Figure 13. A similar sketch of mass and energy balances are presented in this section to calculate a minimum lignin selling price. This section provides all the data used in one scenario that yields a minimum lignin selling price of $829/metric ton. The red rows represent inputs into the process, and the green rows represent streams leaving the process. Numbers in red are assumptions.

4.4.1 Wood chip feed

We model a 1500 ton/day pulp mill production in the Southeastern United States. Assuming a conservative pulp yield of 45.4%, 125,000 kg/hr of dry chips are required. Our feedstock is a juvenile slash pine chip with composition based on analysis of the juvenile slash pine chips from CHAPTER 3. The chip solids are broken up into six categories (cellulose, hexoses, pentoses, lignin, extractives and acetyl) as shown in Table 6.

With a measured 33% lignin and 42% cellulose, we can expect an actual softwood feed to have less lignin and higher cellulose. The assumed moisture content is 50%. The entirety of this feed is added into the system. For this model, the feedstock cost of wood chips is neglected as we assume the value of woodchips remains constant throughout the process. This is based on the idea that yield is maintained in LVPP. For scenarios that

calculated a change in chip value, a market price of $0.6422/kg for dry pulpwood was used (Jackson 2016).

Table 6. Mass flow rates of the wood chips entering the LVPP process.

Stream 1: Initial Chip Stream		
Chip Flow - to Steaming		
Temperature	25	˚C
Dry Input Chips	125,000	kg/hr
Water with Input Chips	50	%
Water with Input Chips	125,000	kg/hr
Total Chips	250,000	kg/hr
Chip Composition		
Species	**Juvenile Slash Pine**	
Cellulose	42	%
Hexoses	14	%
Pentoses	8	%
Lignin	33	%
Extractives	2	%
Acetyl	1	%
Total	100	%

4.4.2 Treatment reactor

The treatment reaction is broken up into a steaming section and a treatment section. The steaming section uses LP steam to heat the woodchips to 125˚C and the treatment section uses MP steam to heat the woodchips to their treatment condition (in this case 185˚C).

4.4.2.1 Steaming section

LP steam is used to treat the wood chips from Stream 1. The amount of steam required is calculated based on its latent heat of vaporization and the specific heats of water and wood chips (Stewart and Thom 1973). A LP steam demand of 45,920 kg/hr includes steam lost during steaming, currently assumed at 10%. The cost of low pressure is assumed

to be $6.60/1000 kg of steam leading to a final operating cost of $303/hr for steaming. No capital costs are considered for this stream because they are combined with the treatment section. Flow rates for the chip steaming section are outlined in Table 7.

Table 7. Mass flow rates and steam demand for chip steaming.

Stream 2: Chip Steaming		
Steam Conditions		
Outlet Temperature	125.0	˚C
Steam Inlet Pressure	1.2	MPa
Steam lost during Steaming	10.0	%
From Stream 1		
Cellulose	52,500	kg/hr
Hexoses	17,500	kg/hr
Pentoses	10,000	kg/hr
Lignin	41,250	kg/hr
Extractives	2,500	kg/hr
Acetyl	1,250	kg/hr
Water	125,000	kg/hr
Total	250,000	kg/hr
Steam Requirement		
Specific heat of chips	2.9	J/g˚C
Specific heat of water	4.2	J/g˚C
Heat Required for Steaming	88.5	GJ/hr
LP Steam, Heat of Vaporization	2.12	MJ/kg
LP Steam Demand	45,920	kg/hr
Chip Mass Flow Out - to Treatment		
Cellulose	52,500	kg/hr
Hexoses	17,500	kg/hr
Pentoses	10,000	kg/hr
Lignin	41,250	kg/hr
Extractives	2,500	kg/hr
Acetyl	1,250	kg/hr
Water	166,328	kg/hr
Total	291,328	kg/hr
Economics		
Cost of LP Steam	6.6	$/1000 kg
Operating Cost	303	$/hr

4.4.2.2 Treatment section

All solids and additional water are sent to the treatment section and heated to 185˚C. The reactor conditions are specified in Table 8. The treatment solvent is HMDA with a density of 840 kg/m^3 and a specific heat of 2.0 J/g˚C.

Table 8. Mass flow rates into reactor and economics for treatment.

Stream 3: Chip Treatment		
Reactor Conditions		
Max Temperature	185.0	˚C
Ramp Time	30	min
Time at Max Temperature	90.0	min
Liquor/Wood Ratio	4	
Solvent Concentration	50.0	%/vol
Outlet Consistency	31	% solids
Mass Flow From Stream 2, Stream 7, and Stream 8		
Solids from 2	125,000	kg/hr
Water from 2	166,328	kg/hr
Water from Stream 7 and Stream 8	83,672	kg/hr
Solvent from Stream 7 and Stream 8	206,501	kg/hr
Required additional solvent	3,499	kg/hr
Total Water	250,000	kg/hr
Total Solvent	210,000	kg/hr
Total Flow	585,000	kg/hr
Energy Conditions		
Specific Heat of Solvent	2.0	J/g˚C
Steam lost during Steaming	0	%
Heat Required for Heat-up	109.4	GJ/hr
MP Steam: Heat of Vaporization	1.994	MJ/kg
MP Steam Demand	54,864	kg/hr
Economics		
Cost of MP Steam	10.50	$/1000 kg
Steam Cost	634	$/hr
Equipment Costs (Andritz)	15	MM$
Installed Costs (3x multiplier)	45	MM$
Cost of Solvent	0.648	$/kg
Feedstock Cost	2,268	$/hr

The treatment conditions of 50% v/v solvent, 185 ˚C, and 90 minutes are based on experimental work from CHAPTER 6. Steam demand is determined based on the heat required for heating up solvent, water, and solids. All solids are assumed to have an average specific heat equal to a wood chip.

MP steam is used to heat the treatment reactor to working temperatures. The amount of steam required is calculated based on its latent heat of vaporization and the specific heats of water, solvent, and wood chips (Stewart and Thom 1973). This MP steam demand of 54,864 kg/hr, assumed to cost $10.5/1000 kg of steam, results in a final steam cost of $634/hr. Solvent is added in this step to make up for all solvent lost in the process. In this scenario, 3,499 kg/hr of solvent are required. The solvent is valued at $0.648/kg based on calculations in SECTION 6.3.3.

The treatment digester was costed by an industry estimate from Andritz. The digesters are sized based on pulp production and 0.6 sizing exponent may be used for varied sizes. For longer residence times, the capital cost would increase. In this scenario we do not assume a larger digester. Installed equipment costs are estimated at 3x the equipment cost.

Treatment effects are based on internal experimental values. For HMDA, a 185˚C treatment held for 90 minutes at maximum temperature results in solid removal rates of 6.3% for cellulose, 21.6% for hexoses, 6.7% for pentoses, 48.4% for lignin, 95% for extractives, and 50% for acetyl. All removed solids are assumed to be dissolved in the solution unless otherwise specified. The resulting mass flows are presented in Table 9.

Table 9. Mass flow rates leaving the treatment reactor.

Stream 3: Chip Treatment (cont.)		
Chip Mass Flow Out - to Washing (Stream 4)		
Cellulose	49,207	kg/hr
Hexoses	13,718	kg/hr
Pentoses	9,330	kg/hr
Lignin	21,296	kg/hr
Extractives	125	kg/hr
Acetyl	625	kg/hr
Total Solids	94,300	kg/hr
Water	165,323	kg/hr
Solvent	138,871	kg/hr
Dissolved Cellulose	2,177	kg/hr
Dissolved Hexoses	2,501	kg/hr
Dissolved Pentoses	443	kg/hr
Dissolved Lignin	13,196	kg/hr
Dissolved Extractives	1,571	kg/hr
Dissolved Acetyl	413	kg/hr
Total Dissolved Solids	20,301	kg/hr
Liquid Flow Out - to Precipitation (Stream 5)		
Dissolved Cellulose	1,115	kg/hr
Dissolved Hexoses	1,281	kg/hr
Dissolved Pentoses	227	kg/hr
Dissolved Lignin	6,759	kg/hr
Dissolved Extractives	804	kg/hr
Dissolved Acetyl	212	kg/hr
Total Dissolved Solids	10,398	kg/hr
Water	84,677	kg/hr
Solvent	71,129	kg/hr
Total	**166,204**	**kg/hr**

4.4.3 Chip Washing

Wood chips leave the digester with an outlet consistency of 31%. Fully saturated with solvent and dissolved solids, a washing step is proposed during the feed to the Kraft digester. A modified feed system is proposed that pulls vacuum and showers the chips with water as they are conveyed up to the top of the Kraft digester. In this scenario, the overall

displacement ratio is assumed to be 0.98 and the dilution factor is 4.5 m^3/metric ton of dry solids. These values are similar to brownstock washing but are likely underestimates because wood chips are harder to wash than fibrous material (Santos and Hart 2014). The chip washing mass flows are presented in Table 10 and Table 11.

Table 10. The inlet flows to the chip washing operation.

Stream 4: Chip Washing		
Reactor Conditions		
Temperature	70.0	˚C
Pressure	1.0	Bar
Dilution Factor	4.5	m^3/metric ton
Overall Displacement Ratio	0.98	
Outlet Consistency	31	% solids
Flow in from Stream 3 and Stream 7		
Cellulose	49,207	kg/hr
Hexoses	13,718	kg/hr
Pentoses	9,330	kg/hr
Lignin	21,296	kg/hr
Extractives	125	kg/hr
Acetyl	625	kg/hr
Total Solids	94,300	kg/hr
Water	165,323	kg/hr
Solvent	138,871	kg/hr
Dissolved Cellulose	2,177	kg/hr
Dissolved Hexoses	2,501	kg/hr
Dissolved Pentoses	443	kg/hr
Dissolved Lignin	13,196	kg/hr
Dissolved Extractives	1,571	kg/hr
Dissolved Acetyl	413	kg/hr
Total Dissolved Solids	20,301	kg/hr
Water Required based on Dilution Factor	424,352	kg/hr
Wash Water from Stream 7	320,251	kg/hr
Dilute Solvent from Stream 7	1,040	kg/hr
Added Water	104,101	kg/hr

Table 11. The mass flows out of chip washing.

Stream 4: Chip Washing cont.		
Chip Mass Flow Out - To Digester (Pulp Mill)		
Cellulose	49,207	kg/hr
Hexoses	13,718	kg/hr
Pentoses	9,330	kg/hr
Lignin	21,296	kg/hr
Extractives	125	kg/hr
Acetyl	625	kg/hr
Total Solids	94,300	kg/hr
Water	301,473	kg/hr
Solvent	2,722	kg/hr
Total Solvent Lost in Washing	**1.30**	**%**
Dissolved Cellulose	43	kg/hr
Dissolved Hexoses	49	kg/hr
Dissolved Pentoses	9	kg/hr
Dissolved Lignin	259	kg/hr
Dissolved Extractives	31	kg/hr
Dissolved Acetyl	8	kg/hr
Total Dissolved Solids Lost	**398**	**kg/hr**
Liquid Flow Out - to Precipitation (Stream 5)		
Dissolved Cellulose	2,135	kg/hr
Dissolved Hexoses	2,452	kg/hr
Dissolved Pentoses	435	kg/hr
Dissolved Lignin	12,937	kg/hr
Dissolved Extractives	1,540	kg/hr
Dissolved Acetyl	405	kg/hr
Total Dissolved Solids	19,904	kg/hr
Water	288,202	kg/hr
Solvent	137,190	kg/hr
Total	**445,295**	**kg/hr**
Solvent Concentration	**36.2**	**% v/v**

Capital costs for this modified digester feed are based on an industrial quote of $3 million from Andritz for a standard feed. An additional $500,000 is added for the vacuum and shower. The total installed capital cost is then $10.5 MM. The capital and energy costs are presented in Table 12.

Table 12. The economics of the treatment unit operation.

Stream 4: Chip Washing cont.		
Energy Conditions		
Energy released while cooling	142.5	GJ/hr
Energy from pressure release	0.44	GJ/hr
Economics		
Electric Power	932	kW-hr
Cost of Electricity	0.06	$/kW-hr
Operating Cost	56	$/hr
Equipment Costs (Andritz)	3.50	MM$
Installed Costs (3x multiplier)	10.50	MM$
Cost of Water	0.0040	$/kg
Feedstock Cost	416	$/hr
Energy produced from pressure release	122	KW-hr
Operating revenue	7.33	$/hr

In this scenario, only the energy from flashing the hot chips and solvent is considered as recyclable. The energy released as the liquid and solids cool during washing is not recovered. The energy savings are assumed to be 0.44 GJ/hr based on pressure drop models in ASPEN+. Electrical power is for the conveyer and vacuum is estimated at 932 kW-hr based on a multiplier of brownstock washing electric power requirements.

4.4.4 Lignin precipitation and washing

The lignin rich solution from treatment and post-wash solution are combined into a precipitation reactor.

4.4.4.1 Precipitation reactor

After precipitation, the solids are washed to create a final lignin product stream. The precipitation reactor consumes CO_2 at an assumed rate of 200 kg/metric ton lignin (Tomani, Axegård et al. 2011). The residence time of the precipitation is assumed to be 60 minutes at 70˚C (Fatehi and Chen 2016). Following precipitation and solid separation, the

lignin solid content is 50%. In this scenario, we assume only lignin precipitates at a yield of 92%. We also assume that all CO_2 is converted to a carbamate as the reaction with the diamine is much faster than the reaction with water (Mondal, Bandyopadhyay et al. 2017). In practice, an equilibrium will be reached with a non-zero partial pressure of CO_2 above the solvent. Equipment costs are estimated based on residence time and volumetric flow rate. In this scenario, the capital costs for a stainless-steel tank is estimated at $322,000. A flowsheet of the inlet flow and economics is presented in Table 13.

Table 13. Inlet flows to the precipitation reactor.

Stream 5: Lignin Precipitation		
Reactor Conditions		
Precipitation Temperature	70.0	˚C
Carbonation Time	60	min
CO_2 Loading	0.200	kg/kg lig
Precipitated solids consistency	50.0	% solids
Assumed conversion to carbamate	100	%
Mass of Chips In From Streams 3 and 4		
Dissolved Cellulose	3,250	kg/hr
Dissolved Hexoses	3,733	kg/hr
Dissolved Pentoses	662	kg/hr
Dissolved Lignin	19,696	kg/hr
Dissolved Extractives	2,344	kg/hr
Dissolved Acetyl	617	kg/hr
Total Dissolved Solids	30,302	kg/hr
Water	372,879	kg/hr
Solvent	208,318	kg/hr
Added CO_2	3,939	kg/hr
Acid Precipitation by Washing		
Lignin	92	%
Precipitation of other dissolved species	0	%
Liquid with precipitated lignin	18,120	kg/hr
Gas Stream Consumed		
Assume all CO_2 goes to Carbamate	3,939	kg/hr
Economics		
CO_2 Price	0.025	$/kg
CO_2 Feedstock Cost	98	$/hr
Equipment Costs	0.322	MM$
Installed Costs	0.966	MM$

Based on the solid content of the precipitated lignin, the liquid and dissolved solids are proportionally distributed as presented in Table 14.

Table 14. The outlet flows of the precipitation reactor.

Stream 5: Lignin Precipitation cont.		
Solid Lignin Flow Out - to Lignin Washing (Stream 6)		
Dissolved Cellulose	101	kg/hr
Dissolved Hexoses	116	kg/hr
Dissolved Pentoses	21	kg/hr
Dissolved Lignin	49	kg/hr
Dissolved Extractives	73	kg/hr
Dissolved Acetyl	19	kg/hr
Dissolved Carbamate	447	kg/hr
Total Dissolved Solids	827	kg/hr
Water	11,625	kg/hr
Solvent	6,170	kg/hr
Lignin Solids	18,120	kg/hr
Total	37,570	kg/hr
Liquid Stream - to Distillation (Stream 7)		
Dissolved Cellulose	3,149	kg/hr
Dissolved Hexoses	3,617	kg/hr
Dissolved Pentoses	641	kg/hr
Dissolved Lignin	1,527	kg/hr
Dissolved Extractives	2,271	kg/hr
Dissolved Acetyl	598	kg/hr
Dissolved Carbamate	13,893	kg/hr
Total Dissolved Solids	25,695	kg/hr
Water	361,253	kg/hr
Solvent	191,746	kg/hr
Total	**578,694**	**kg/hr**
Solvent Concentration	**38.7**	**% v/v**
Dissolved Solid Concentration	**4.4**	**% mass**

4.4.4.2 Lignin washing tank

The lignin solids are sent to a smaller lignin washing tank that recovers the lignin. The capital for this small tank is estimated at $113,000 for a total volumetric flowrate of less than 75,000 kg/hr. The required water is estimated from lignin washing performed by

Innventia (Axegård, Berglin et al. 2011). An assumed 466 kW-hr of electric power is required to power the rotary lignin washer (Kautto, Realff et al. 2013). A flowsheet of the inlet flows and economics is presented in Table 15.

Table 15. The inlet flows to the lignin washer.

Stream 6: Lignin Washing		
Conditions		
Precipitation Temperature	70.0	˚C
Displacement Ratio	0.95	
Solid Lignin Consistency	50	% solids
Wash Water Needed	2	kg/kg lignin
Mass flow in from Stream 5		
Dissolved Cellulose	101	kg/hr
Dissolved Hexoses	116	kg/hr
Dissolved Pentoses	21	kg/hr
Dissolved Lignin	49	kg/hr
Dissolved Extractives	73	kg/hr
Dissolved Acetyl	19	kg/hr
Dissolved Carbamate	447	kg/hr
Total Dissolved Solids	827	kg/hr
Lignin	18,120	kg/hr
Water	11,625	kg/hr
Solvent	6,170	kg/hr
Added Water	36,240	kg/hr
Economics		
Electric Power	466	kW-hr
Cost of Electricity	0.06	$/kW-hr
Energy Cost	28	$/hr
Equipment Costs	0.113	MM$
Installed Costs	0.339	MM$
Feedstock (Added Water) Cost	145	$/hr

With an assumed displacement ratio of 0.95, the solid lignin product from Stream 6 is relatively pure. The wash stream is sent to the distillation unit for further solvent recovery. These two outlet streams are described in Table 16.

Table 16. The outlet flows from the lignin washer.

Stream 6: Lignin Washing Cont.		
Solid Lignin Flow Out (Product Stream)		
Dissolved Cellulose	5.1	kg/hr
Dissolved Hexoses	5.8	kg/hr
Dissolved Pentoses	1.0	kg/hr
Dissolved Lignin	2.5	kg/hr
Dissolved Extractives	3.7	kg/hr
Dissolved Acetyl	1.0	kg/hr
Dissolved Carbamate	22.4	kg/hr
Total Dissolved Solids	41.3	kg/hr
Lignin Solids	18,120	kg/hr
Water	17,812	kg/hr
Solvent	309	kg/hr
Total	36,282	kg/hr
Liquid Stream to Distillation (Stream 7)		
Dissolved Cellulose	96	kg/hr
Dissolved Hexoses	111	kg/hr
Dissolved Pentoses	20	kg/hr
Dissolved Lignin	47	kg/hr
Dissolved Extractives	69	kg/hr
Dissolved Acetyl	18	kg/hr
Dissolved Carbamate	425	kg/hr
Total Dissolved Solids	786	kg/hr
Water	30,054	kg/hr
Solvent	5,862	kg/hr
Total	**36,701**	**kg/hr**

4.4.5 Distillation and Stillage

Exit streams from stream 6 and stream 7, consisting mainly of solvent and water, are sent to the distillation column to concentrate the solvent sufficiently for treatment in Stream 3. To account for the dissolved solids that enter the distillation column, we assume a full precipitation of these solids in the stillage, or bottom of the column, for this scenario. This assumption is a simplifying one, but for a mass balance perspective, the dissolved solids in a recycle loop will eventually precipitate out at a rate equal to the inlet feed.

4.4.5.1 Distillation column

The constraints for the distillation column are described in Table 17. We assume a 100% solvent recovery from the carbamate species and a sequestration of CO_2 after condensing.

Table 17. Distillation column flowrates and specifications.

Stream 7: Distillation of solvent		
Conditions		
Solvent Recovery	99.5	%
Required concentration for treatment (Stream 2)	**77.615**	**%/vol**
Assumed solids that precipitate out	100.0	%
Assumed solid consistency	50	% solids
Assumed carbamate reversal	100	%
Inlet feed from Stream 5 and Stream 6		
Dissolved Cellulose	3,245	kg/hr
Dissolved Hexoses	3,727	kg/hr
Dissolved Pentoses	661	kg/hr
Dissolved Lignin	1,573	kg/hr
Dissolved Extractives	2,341	kg/hr
Dissolved Acetyl	616	kg/hr
Dissolved Carbamates	14,317	kg/hr
Total Dissolved Solids	26,480	kg/hr
Water	391,307	kg/hr
Solvent	207,993	kg/hr
Inlet Solvent Concentration	**38.75**	%
Solids Flow Out (Very Bottom) - to Stillage Washing (Stream 8)		
Waste Solids	12,163	kg/hr
Waste Liquid	12,163	kg/hr
Assume concentration same as bottoms	77.615	%/vol
Solvent	9054	kg/hr
Water	3109	kg/hr
Total	24,325	kg/hr
Water Stream (Top) to Chip Washing (Stream 4)		
Dissolved Solids	0	kg/hr
Solvent	1,040	kg/hr
Water	320,251	kg/hr
Solvent Stream (Bottom) - Recycled to Treatment (Stream 3)		
Dissolved Solids	0	kg/hr
Solvent	197,899	kg/hr
Water	67,948	kg/hr
Total	265,847	kg/hr
CO_2 Stream – Sequestered (Product Stream)		
CO_2	3933	kg/hr

Utility costs were calculated from an ASPEN+ simulation using a RadFrac column and the specifications from Stream 7. Of note, the CO_2 released from the HMDA carbamate requires an energy cost of 92 kJ/mol CO_2.This energy release was not considered during lignin precipitation, but it is added to the heat duty of the distillation column. A list of ASPEN+ input settings are presented in Table 18. Based on distillation sizing constraints, two distillation columns are needed. Therefore, the feed was halved, and the results presented are based on a single column.

Table 18. Settings for ASPEN+ simulations.

ASPEN+ V9 Model			
Properties			
Component Databank	"Hexamethylenediamine" & "Water"		APV90.PURE35
Property Method	NRTL		Common
Binary Interactions	-504.368 (BIJ), 757.955 (BJI), 0.3 (CIJ), 25˚C (TLOWER), 25˚C (TUPPER)		UNIFAC R-PCES
Feed			
Mass Flow of Water	195654 kg/hr	**Temperature**	70 ˚C
Mass Flow of HMDA	103997 kg/hr	**Pressure**	1 atm
RadFrac			
Calculation Type	Equilibrium	**Feed Stream**	Stage 16
Number of Stages	20	**Convention**	Above-Stage
Condenser	Partial-Vapor	**Stage 1**	Vapor
Reboiler	Kettle	**Stage 20**	Liquid
Valid phases	Vapor-Liquid	**Stage 1 Pressure**	1 atm
Convergence	Standard	**Design Specifications**	
Reflux ratio	0.0506035	**Mass Recovery**	0.995
Distillate to feed ratio	0.784423	**Mass Purity**	0.77615
Mass Reflux Ratio	0.001 to 5	**Mass D/F Ratio**	0.01 to 2
Convergence		**Block Options**	
Algorithm	Standard	**Simulation**	True components
Maximum iterations	100	**Free-water phase**	STEAM-TA
Initialization Method	Standard	**Water solubility**	3 - No correction

Based on the inputs outlined in Table 18, the simulation results are presented in Table 19.

Table 19. Stream results for RadFrac distillation column.

Condenser			
Temperature	100.55 ˚C	**Reflux Rate**	5154.05 kg/hr
Heat Duty	-3.1 MW	**Reflux Ratio**	0.0309869
Distillate Rate	166,330 kg/hr	**D/F Ratio**	0.55508
Heat Transfer Area	57.955 m^2	**Equipment Cost**	$19,600
Tube gauge pressure	4.16 barg	**Shell gauge pressure**	2.43 barg
Tube operating temp	35˚C	**Shell operating temp**	101.02 ˚C
Tube outside diameter	0.0254 m	**Tube length extended**	6.10 m
Condenser Accumulator			
Liquid Volume	112 m^3	**Equipment Cost**	$60,000
Vessel Diameter	3.66 m	**Gauge pressure**	1.034 barg
Vessel Length	10.67 m	**Operating temp**	100.55 ˚C
Reboiler			
Temperature	114.657	**Boilup Rate**	203,437 kg/hr
Heat Duty	117.90 MW	**Boilup ratio**	1.52593
Bottoms Rate	133,320 kg/hr	**B/F Ratio**	0.463691
Heat Transfer Area	2934.57 m^2	**Equipment Cost**	$679,900
Tube gauge pressure	7.605 barg	**Shell gauge pressure**	4.73 barg
Tube operating temp	164.3 ˚C	**Shell operating temp**	114.66 ˚C
Tube outside diameter	0.0254 m	**Tube length extended**	6.10 m
Reflux pump			
Pump efficiency	0.7	**Equipment Cost**	$5,200
Liquid Flow Rate	6.44 m^3/hr	**Design pressure**	1.034 barg
Bottom Stream		**Top Stream**	
Water	29844 kg/hr	**Water**	165810 kg/hr
HMDA	103477 kg/hr	**HMDA**	520 kg /hr
Surface Tension	43.9869 dyne/cm	**Volume Flow**	282378 m^3/hr
Mass Density	738.392 kg/m^3	**Mass Density**	0.589033 kg/m^3
Inlet Volumetric Flow		354.229 m^3/hr	

We double the reboiler heat duty from Table 19 to account for both columns and we add the energy consumed by CO_2 desorption (92 kJ/mol CO_2) to calculate steam demand. Total energy consumed by CO_2 is 2.284 MW, so total energy requirement is 238 MW which corresponds to a 429,801 kg/hr MP steam requirement or 4,513 $/hr for steam.

Capital costs for reboiler, condenser, condenser accumulator, and reflux pump are modeled in ASPEN+ and displayed in Table 19. After doubling these costs, the total equipment costs for these parts are $764,700. Capital costs for the distillation towers are calculated as per SECTION 5.2.1 and APPENDIX D. In short, the diameter of the distillation columns was obtained from the mass flow rates and density by the method described by Fair (Fair 19). For this scenario, the calculated diameter was 4.46 m and a height of 21.03 m was calculated based on an assumed plate separation of 36". The bare-module equipment cost was calculated as per APPENDIX D with the assumptions of a stainless-steel column, sieve tray type, and a column thickness of 2.5 cm. For this scenario, the bare module cost was $4.157 MM per column, or a combined equipment cost of $8.314 MM for the towers. Total equipment costs for the distillation unit are $9.078 MM and the installed cost is $27.234 MM.

4.4.5.2 Stillage, solids washing

Similar to the washing of lignin in Stream 6, the precipitated solids from the distillation unit must be washed to recover valuable solvent. This work assumes that washing does not cause re-precipitation, and we assume all the same washing conditions and efficacy as Stream 6. The inlet flow to the stillage washing is presented in Table 20. With a lower flow rate, the equipment cost for a stainless-steel tank is $84,000.

The solvent recovered from this washing stage are used for treatment in stream 3. The solids from this stream are sent to the recovery boiler. The energy value from this stream is presented but not included in economic calculations, as it has no marginal benefit compared to the pulp mill where it would have been burned anyways in the recovery boiler. This solids stream is presented in Table 20 and Table 21.

Table 20. The inlet flows to the stillage, solids washing.

Stream 8: Stillage, Solids Washing		
Conditions		
Temperature	70	˚C
Displacement Ratio	0.95	
Added Water	2	kg/kg solids
Assumed solid consistency	50	% solids
Assumed Dissolved Solids in Wash Stream	0.0	% inlet solid
Mass Flow in From Stream 7		
Waste Solids	12,163	kg/hr
Waste Liquid	12,163	kg/hr
Solvent	9,054	kg/hr
Water	3,109	kg/hr
Total	24,325	kg/hr
Added Water	24,325	kg/hr
Economics		
Electric Power	233	kW-hr
Cost of Electricity	0.06	$/kW-hr
Energy Cost	14	$/hr
Equipment Costs	0.083	MM$
Installed Costs	0.249	MM$
Feedstock (Added Water) Cost	97	$/hr

Table 21. The outlet flows from the stillage, solids washing.

Stream 8: Stillage, Solids Washing Cont.		
Washed Solids -> Burned		
Solids	12,163	kg/hr
Solvent	571	kg/hr
Water	11,592	kg/hr
Water Heat of vaporization	2,260	KJ/kg
Heat of combustion solids	18.4	MJ/kg
Heat of combustion solvent	28	MJ/kg
Heat to boil off water	27,651	MJ/hr
Heat of combustion	240,003	MJ/hr
Total Energy Produced	58,991	kW-hr
Flowthrough - Recycled to Treatment (Stream 3)		
Total Dissolved Solids	0	kg/hr
Water	16050	kg/hr
Solvent	10845	kg/hr
Total	26895	kg/hr

4.4.6 Lignin selling price calculations

To calculate a lignin selling price, the capital and operating costs are compiled together. Once compiled, a net asset value calculation can elucidate a minimum lignin selling price. All capital and operating costs are outlined in Table 22.

Table 22. The process capital and operating costs.

Costs		
Energy Costs	**Cost [$/hr]**	**Stream**
LP Steam for Chip Steaming	303	2
MP Steam for Treatment	576	3
Electricity for Chip Washing	56	4
Electricity for Lignin Washing	28	6
MP Steam for Distillation	4,513	7
Electricity for Stillage Solid Washing	14	8
Total	5,490	$/hr
Material Costs	**Cost [$/hr]**	**Stream**
Additional Solvent for Treatment	2,268	3
Added Water for Chip Washing	416	4
Added CO2 for Precipitation	98	5
Added Water for Lignin Washing	145	6
Added Water for Stillage Solid Washing	97	8
Total	3,025	$/hr
Installed Capital Costs	**Cost [$ MM]**	**Stream**
Chip Digester	45	1-3
Chip Washer	10.5	4
Precipitation Reactor	0.97	5
Lignin Washer	0.34	6
Distillation Column	27.2	7
Stillage Solid Washer	0.25	8
Total	84.3	$ MM

Given a lignin production stream of 18,120 kg/hr, the minimum lignin selling price may be calculated given the assumptions outlined in Table 23.

Table 23. Assumptions for net asset value calculation.

Remaining Assumptions		
Maintenance Cost	15%	With respect to capital costs
Depreciation	10%	Straight
Tax Rate	25%	Percent
Required IRR	25%	Percent
Operating Days	350	Days
Lost lignin heat value	1,443	$/hr

The calculated revenue from the lignin production stream is reduced by a calculated lost lignin heat value of $1,443/hr. This lost heat value is based on a lignin energy value of 28.5 MJ/kg and a natural gas replacement cost of $2.95/mmbtu. Given these assumptions, a minimum lignin selling price of $0.829/kg is calculated. The discounted cash flows for each year are presented in Table 24.

Table 24. Annual discounted cash flow for LVPP scenario.

Year	Discounted Cash Flow
1	$(67,039,000.96)
2	$13,808,799.23
3	$11,047,039.38
4	$8,837,631.51
5	$7,070,105.21
6	$5,656,084.16
7	$4,524,867.33
8	$3,619,893.87
9	$2,895,915.09
10	$2,316,732.07
11	$1,627,094.57
12	$1,301,675.66
13	$1,041,340.52
14	$833,072.42
15	$666,457.94
16	$533,166.35
17	$426,533.08
18	$341,226.46
19	$272,981.17
20	$218,384.94
Total	$0.00

4.5 Conclusions

A preliminary process flow sheet sketch for LVPP, along with a corresponding techno-economic analysis, has highlighted the key assumptions that govern viability of the process. The process assumptions in this analysis are based on current pulp mill processes and other experimental results. These assumptions have not been validated for HMDA, but the economic analysis helps direct the focus of further research. It is evident from the sensitivity analysis that chip washing and the solvent displacement ratio must be understood. The carbamate formation and precipitation of lignin is the second most important assumption to develop. Finally, the experimental results of biomass removal and selectivity must be solidified through further experimentation. Each of these assumptions will require significant research to fully develop an understanding for the LVPP unit operation.

An understanding of these parameters will determine how much higher the minimum lignin selling price will get. What is evident is that the selling price of lignin is highly dependent on the operating costs. Although solvent loss is a major factor, the extraordinary energy required to regenerate the solvent from water is the main economic driver. Towards reducing the current lignin selling prediction of $829/metric ton, an improved understanding of solvent separation must be addressed. Three solvent separation techniques are discussed in CHAPTER 5. With a selling price that will not approach that of Kraft lignin, estimated between $250 - $500/ton (de Assis, Greca et al. 2018), an increased understanding of LVPP lignin's marginal benefit will guide the economic argument for future technical advancement.

CHAPTER 5. TECHNO-ECONOMIC ANALYSIS OF SOLVENT RECOVERY WITH WATER PRECIPITATION

5.1 Introduction

As outlined in CHAPTER 4, the major cost of LVPP is the solvent recovery from a majority water mixture. Another major technology barrier is lignin precipitation from the treatment solvent. This chapter explores these two research questions by addressing precipitation by dilution, or water precipitation.

Integrating lignin and solvent recovery into the larger LVPP process falls into a class of problems where the key concerns are optimizing resource use and minimizing cost. This concept of mass integration was first introduced for separation processes that involve a mass exchange agent, such as liquid-liquid extraction, adsorption (El-Halwagi and Manousiouthakis 1989). Since its introduction, it has since been applied in various chemical industries, including the pulp and paper industry to optimize resource use (Atkins, Walmsley et al. 2012).

Lignin recovery by water dilution has been proposed in several recent publications. Water precipitation is considered for a system that precipitates poplar lignin from an aqueous *p*-toluenesulfonic acid solution (Chen, Dou et al. 2017). Similarly, the black liquor from an acetic acid treatment of *Eucalyptus globulus* is precipitated through water washing (Ligero, Villaverde et al. 2008). At a larger scale, an ethanol Organosolv treatment precipitates lignin with a batch rectification column (Laure, Leschinsky et al. 2014). Following treatment, solvent-saturated biomass is washed with solvent and water to extract the entrained lignin from biomass and precipitate the solubilized lignin. This mixture is

then separated to recover solvent and produce a valuable lignin stream. However, water precipitation requires the lignin-containing solution to be diluted to low solvent concentrations. For most water precipitation methods, the solvent concentration must be diluted to ~10% (Chen, Dou et al. 2017). This dilution creates a high-volume, dilute solvent stream that poses a difficult challenge for industrial processes to separate effectively. For typical pulp mill flows of at least 1000 air-dry tons/day (10% moisture), some biomass pretreatment processes could require separation of over 11 million kg/hr of water from 600,000 kg/hr of solvent. Most processes with water precipitation will still require at least 2 million kg/hr of water based on a 4:1 liquor-to-wood ratio and a solvent concentration of 70%, both of which are ambitious targets for these pretreatment processes.

To understand the feasibility of water precipitation for LVPP, we note the importance of overall solvent recovery. As described in SECTION 4.3.2, the solvent lost in the process is the main economic driver. High solvent recovery in economic models is standard for biorefinery simulations with values of 2% (Chum, Douglas et al. 1985), 1% (Viell, Harwardt et al. 2013, Nitzsche, Budzinski et al. 2016), or even 0.5% solvent loss (Mesa, López et al. 2016). In this work, we model unit operations to concentrate a dilute solvent stream by separating the solvent from water. In this scenario, outlined in Figure 15, both the recovered solvent and water streams are recycled back into the process. Therefore, the separation operation does not directly contribute to solvent loss. We impose a constraint of no more than 2% solvent loss to the water stream and track the concentration of solvent in any recycle stream. However, the scope of this chapter is limited to the water dilution and separation step. Therefore, solvent losses in other areas of the process are not included in these operating costs.

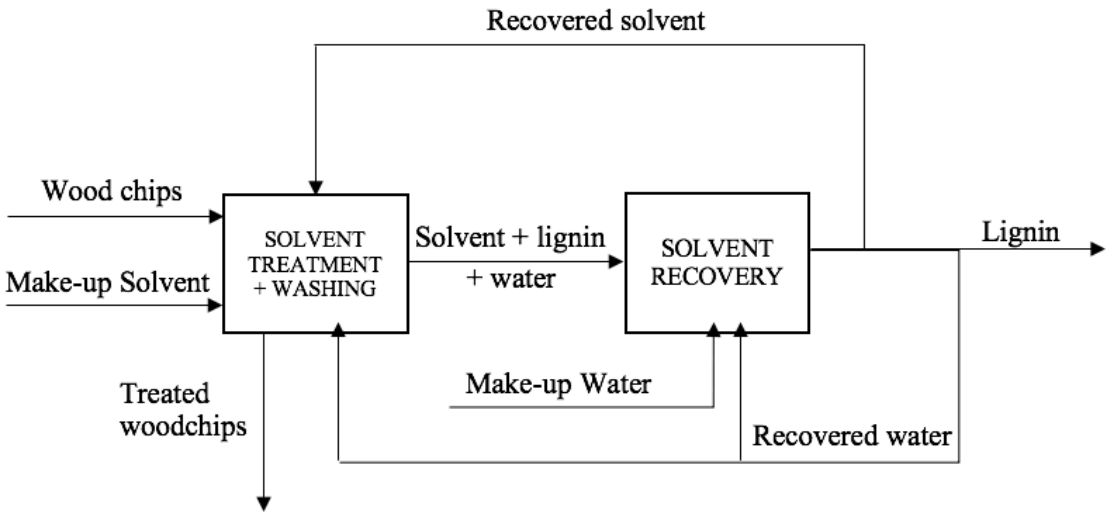


Figure 15. Process flow diagram of LVPP process, including solvent washing and water dilution.

Solvent purity is another factor to consider in the separation process. Here we targeted two different solvent concentration levels: the maximum possible solvent purity achievable and 70% solvent concentration. The 70% solvent target was chosen based on Organosolv process conditions (Ni and Hu 1995) and because of the downstream reduction in separation costs with lower solvent loadings.

Three industrial separation techniques are distillation, reverse osmosis, and multi-effect evaporation. Each of these processes has well-defined models to calculate capital and energy costs associated with the separation (Seider, Seader et al. 2009). In this work, we explore the limitations of individual techniques in solvent recovery for LVPP and describe the ranges of solvent concentration best suited for each technique. Using a techno-economic analysis, we explore multi-step recovery processes that combine two or three methods to achieve desired solvent purity and recovery levels. This analysis provides separation costs per kilogram of lignin produced and enables informed selections of separation techniques.

Herein we describe the associated costs for the concentration of a representative low-boiling solvent (ethanol) and a representative high boiling solvent (DMSO). Both solvents are implicated in biomass processing (Wildschut, Smit et al. 2013, Andanson, Bordes et al. 2014), and their boiling points differ significantly enough from water that separation by temperature difference would be feasible, excepting high ethanol concentrations due to the azeotrope. We provide a sensitivity analysis for the key solvent parameters that can be applied to a variety of different LVPP solvents.

5.2 Methods

5.2.1 Economic Models

Both the total installed cost and the operating cost of each unit were considered. The correlations for installed costs and utility costs were taken from a design textbook and are listed in APPENDIX E. Several assumptions were made throughout the cost calculation process and are detailed in this section.

The installed cost correlations are for the year 2006 (CE index = 500), and at the time of computation the most recent value of CE index available is for 2016 (CE index = 541.7) (Seider, Seader et al. 2009, Jenkins 2018). This CE index is used to estimate a more up-to-date value for the installed cost. Since our system is mostly water, 316 stainless steel is used as a building material for all units to avoid rust formation in the equipment. The flow rate of solvent itself remains constant throughout the calculations (5,600 metric tons/day, corresponding to 233,333 kg/hr).

A reverse osmosis membrane to reject the solvent and allow the passage of water is used. We use parameters for costs and permeance for membranes that are derived from

existing membrane materials. For costing purposes, a Thin Film Composite (TFC) polyamide membrane is assumed, and the membrane price of $35.19/m^2 is obtained from commercial vendors (ForeverPure 2018). The area of the membrane is calculated using the procedure detailed in a separations textbook (Seader, Henley et al. 1998). The permeance value depends on each solvent being tested. For this work, a value of 33.08 kg/(hr m^2 atm) was picked based on the permeance of water through a polyacrylamide membrane (Kanchanalai, Lively et al. 2013). It is assumed that the membrane is replaced yearly to maintain high performance, so the annual cost of membrane replacement is added to the utilities needed by the pump/motor as listed in ASPEN+. The reverse osmosis unit cost is made up of the costs of three components: the membrane itself, the centrifugal pump used to provide pressure difference across the membrane, and the motor that drives the pump. The operating cost is calculated based on the energy needed by the pump to pressurize the feed stream and cost of membrane replacement.

The multi-effect evaporator unit is assumed to have five effects running counter-current and is made up of long-tube vertical evaporators for the highest heat transfer coefficient (Wildschut, Smit et al. 2013). This is similar to what is used in many pulp mills. A supersaturated steam inlet at 130°C and 2 atm provides the required energy to the first effect, while the feed enters from the last effect. Evaporators are not used with low-boiling solvents because too much solvent enters the waste water stream instead of the solvent product stream, violating the 2% solvent loss constraint.

The dimensions of distillation columns were obtained using the method described by Fair with an assumed plate separation of 36” (Fair 1997). The column weight is estimated by assuming a hollow column with the minimum column thickness specified by

Seider (Seider, Seader et al. 2009). Sieve trays are used in the column due to their low-cost and versatility. The tray efficiency is assumed to be 60% based on published efficiency values for similar distillation systems (Bastidas, Parra et al. 2012). The diameter of each column is limited to 4.5 m for ease of transportation to a plant site.

In calculating the capital cost of each unit, we assume that only the installed costs of each unit count towards the total capital investment and only the utility (and membrane) costs count towards the annual operating cost. In other words, factors such as the cost of land, employees, or royalties are not considered as these would be relatively small contributions and constant across all the processes considered here. Thus, the estimated costs may be regarded as lower bounds given the process performance.

Assuming a feed of 2,000 ton/day of woodchips, 40% solvation of the native lignin (Watkins, Nuruddin et al. 2015), an annual process operation of 328 days (Seider, Seader et al. 2009), and full extraction and precipitation of solvated lignin, a lignin production rate of ~80,000 metric tons/year can be obtained. The solvent flow rate is kept constant at 233,333 kg/h (about 5,600 metric tons/year).

To compare the economic feasibility of each unit, an annual total cost was calculated assuming a service life of 20 years. A full breakdown of the calculation is given in APPENDIX D.

The total solvent flow rate in the recovered solvent stream is calculated from the known feed solvent flow rate and the recovery rate of each step in the separation process. This is then subtracted from the feed flow rate to obtain the amount of solvent that ends up in the recovered water stream. The amount of water in the recovered water stream is known based on the start and target solvent concentrations.

5.2.2 ASPEN+ Simulations

A simulation of the process was designed in ASPEN+ to calculate the separation efficiency and utilities required by each unit operation. The distillation columns were modeled using a RADFRAC process model, with a total condenser and reboiler which requires two specifications in addition to the feed location: the recovery and purity of the solvent. Although our process economics assume perfect lignin precipitation, we design our columns to account for residual undissolved lignin in the feed stream. This necessitates a feed stage at the bottom of the column, to limit the chance of fouling of the distillation column trays, particularly in the case of a light boiling solvent. The mass recovery is specified at 0.995, and the mass purity is set to the desired solvent concentration in the product. The reflux ratio and distillate-to-feed ratio are then optimized in the model. The Energy & Cost Analyzer add-on in ASPEN+ gives an estimate of the utility costs involved, while sizing of the column is conducted.

The membrane itself was not part of the simulation, but the pump used to drive fluid flow through the membrane was included. The pressure difference is the same value specified for the membrane. After running the simulation, utility values for the pump are obtained.

The evaporator was assembled using a combination of FLASH2 columns and HEATER units in a counter-current configuration (Vazquez-Rojas, Garfias-Vásquez et al. 2018). The steam released from each flash column is fed into the heater unit, and the resulting energy is fed into the following column. A stream of supersaturated steam is passed through a heater unit to provide the energy input required to run the first flash

column of the operation. The heat duty of each heater approximates the size of each effect to obtain utility values.

A unique simulation for each solvent ensures that the specifications of each unit operation are optimized for the solvent. Process flowsheet diagrams and stream tables are provided for each case in APPENDIX D.

5.3 Results and Discussion

5.3.1 Physical restrictions of individual methods

For each of these three methods, there are limitations on the allowed feed and achievable solvent purity based on chemical engineering practice or physical restrictions on the system.

Distillation is a common separation method for organic solvent recovery in biomass treatment processes (Shuai and Luterbacher 2016). The main limitation on distillation columns is their diameter, which is limited in this study to a maximum value of 4.5 m (or 15 ft). Given a fixed solvent flow rate, Table 25 shows the minimum feed concentration where separation can occur using a specified number of columns to meet the diameter constraint. Processes with more than 5 columns in parallel are not realistic for LVPP and are eliminated from consideration.

Table 25. Minimum feed concentrations for 99.5% mass recovery given a fixed number of columns and a product concentration.

	High-boiling solvent		Low-boiling solvent	
Target product %	70%	90%	70%	90%
1 column	48%	56%	64%	88%
2 columns	34%	38%	49%	58%
3 columns	27%	29%	40%	46%
4 columns	22%	23%	34%	37%
5 columns	18%	20%	29%	32%
10 columns	11%	11%	17%	18%

An alternative separation method to distillation columns is evaporators when the boiling points of the solvent and water are sufficiently different. Evaporators are commonly-used in the pulping industry for black liquor recovery. This separation unit is effective at processing large volumetric flowrates, but its efficacy is dependent on an easy separation from water. Acting effectively as a single-stage distillation column, this technique should only be used for high boiling solvents with relative volatilities >>1 (Figure D.2). For these solvents, the highest solvent recovery possible in an evaporator is 99%. Low-boiling solvents act similarly to the high-boiling solvents with low relative volatilities and have a maximum recovery of 30%, so the use of evaporators is limited to high-boiling solvents with high relative volatilities. As shown in Figure 16, increasing the initial feed solvent concentration for these types of solvents improves solvent recovery at any given threshold concentration.

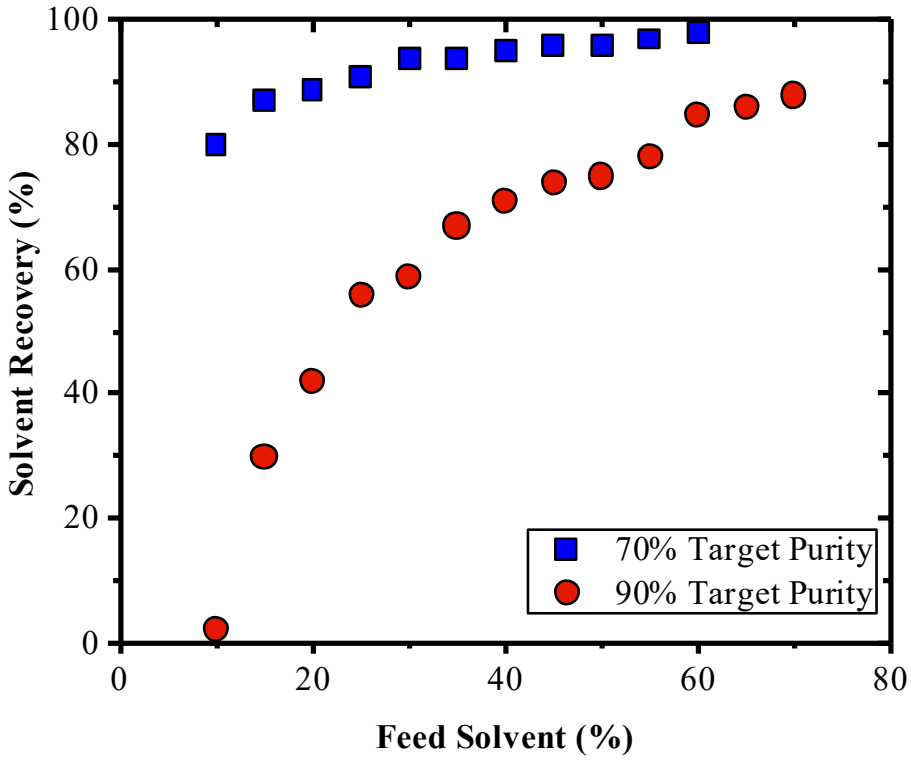


Figure 16. Achievable solvent recovery for evaporator unit at various feed concentrations. Solvent used is DMSO (a high-boiling, high-relative volatility solvent).

Currently, membranes are not widely utilized in the pulping industry, but there is precedence for using membranes to separate organic solvents from water. While available, current solvent-water membranes often have rejection levels much lower than desalination membranes (Koyama, Nishi et al. 1982, Kirk-Othmer 2004). Though rejection levels are anticipated to improve, we use published values for solvent rejection in this work (Kirk-Othmer 2004). Another constraint for membranes is the hydraulic pressure limit of 80 atm. Based on standard engineering practice, we cap the osmotic pressure at 70 atm when calculating the maximum retentate concentration. Assuming a non-constant pressure driving force (see APPENDIX D), the retentate osmotic pressure is fixed and corresponds

to a solvent concentration of 24% and 13% for high-boiling and low-boiling solvents, respectively.

5.3.2 Comparison of possible processes

Given the restrictions present in each method, a few possible processes are presented that take a feed of 10% solvent and achieve the target concentrations of 70% and 90%. Multi-step separation processes are included in the present work and well-documented in literature (Frolkova and Raeva 2010, Kanchanalai, Lively et al. 2013, Sholl and Lively 2016). The considered process configurations are:

- The single-method option
- The highest solvent recovery option
- The lowest cost option without membranes
- The lowest cost option with membranes

Figure 17 shows the trade-off between solvent recovery and overall cost. The cheapest option has the lowest solvent recovery, so an optimal selection could be the third option in each group. This option keeps costs under $1.50/kg and solvent % in recovered water at 0.5 %. Using all three methods sequentially yields neither the lowest cost nor the highest recovery, so three-method processes are not presented here.

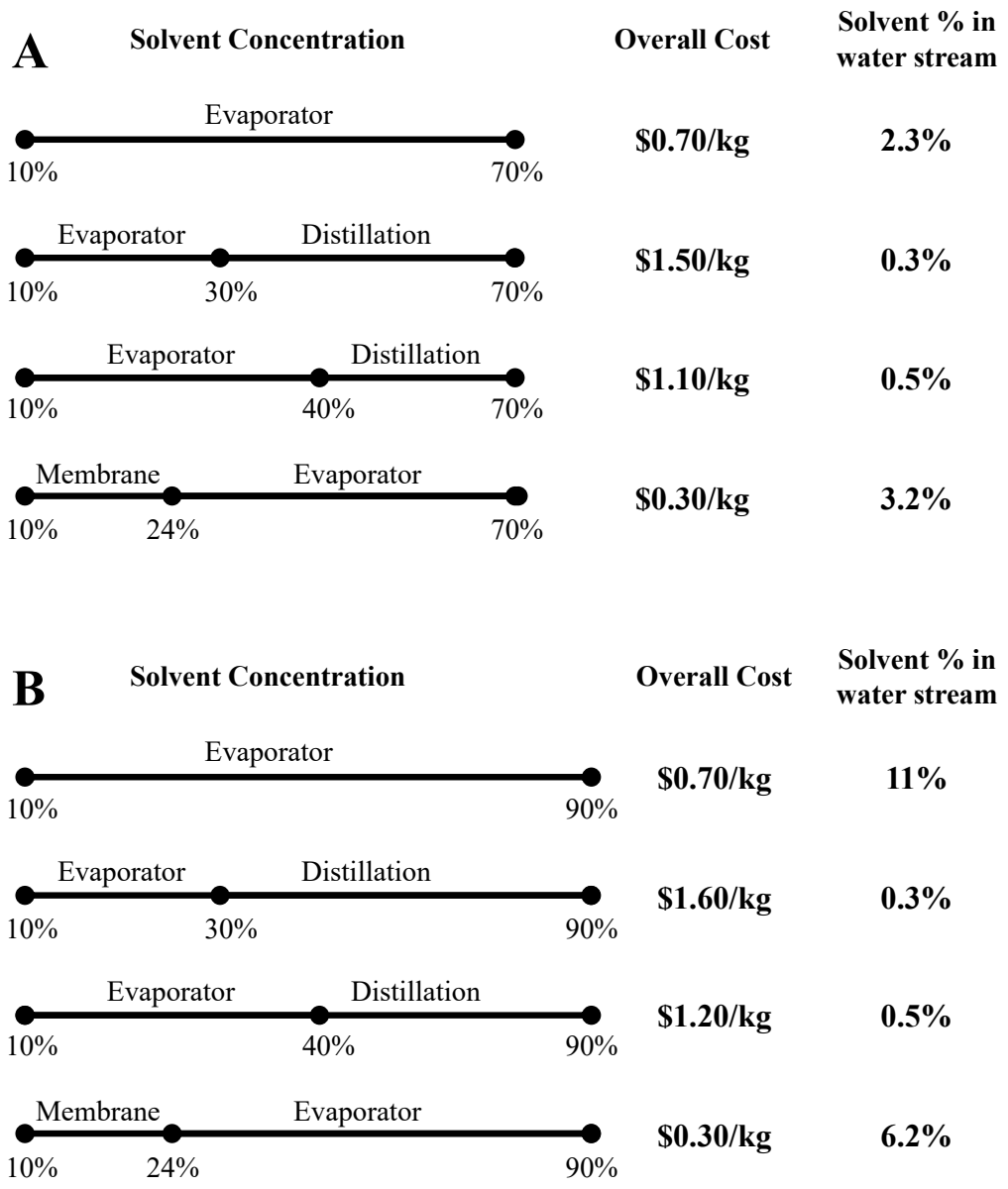


Figure 17 - Possible processes to achieve (A) 70% solvent and (B) 90% solvent purities for high-boiling solvents. The options presented are: single-method, highest solvent recovery, lowest cost without membrane, and lowest cost with membrane.

For a low-boiling solvent, we must use distillation columns to obtain a solvent recovery above the 30% possible with evaporators. However, distillation column constraints require a feed concentration of at least 30% which creates a gap between the maximum product concentration achievable by membranes (13%) and the minimum feed

concentration allowable for a 5-column distillation series (~30%). This gap suggests that water precipitation and subsequent solvent separation of a low-boiling solvent from water is both economically and technically infeasible. A lower solvent flow rate of 176,223 kg/hr would be required while maintaining a feed concentration of 10%. The cost of a two-step, membrane and distillation separation to achieve 70% purity would translate to $3.00/kg of lignin and could only process 1,500 ton/day of woodchips. For most low-boiling solvents, an alternative to water-precipitation is a direct evaporation of solvent from lignin. This is not in the scope of this economic analysis but is addressed in SECTION 5.3.4.

5.3.3 Factors Affecting Cost

We looked at several factors throughout the whole process that might affect either capital or operating costs and at the significance of each factor.

5.3.3.1 Permeance of reverse osmosis membrane

In the present work, we assume a fixed permeance value because the value is dependent on the specific solvent/membrane material combination chosen. To see the impact of this decision on the overall process, the annual total costs for three membranes were compared: one with the original permeance value P, one with a permeance of 2P, and one with a permeance of 0.5P. These changes result in cost changes of less than $0.01/kg lignin, indicating the membrane costs are not the main driver of the overall economics.

5.3.3.2 Rejection of reverse osmosis membrane

In this study we assume a membrane rejection of 80% for the high-boiling solvent and 45% for the low-boiling. These values are typically seen in literature for organic solvent/water membrane separations (Koyama, Nishi et al. 1982). To see the impact of

membrane rejection on the overall process, the annual total costs for a membrane with 80% rejection is compared to that for a hypothetical membrane with 98% rejection. Although the amount of solvent that ends up in the recovered water stream is significantly higher for the membrane with the lower rejection rate, the total annual costs are very similar.

5.3.3.3 Solvent Choice – Relative Volatility and Azeotropes

The choice of solvents used in the process depends on their efficiency in lignin removal. That choice informs how easily the various separation units are able to recover the solvents. For this analysis, the effects of the relative volatility of solvents and the presence of azeotropes on separation units will be discussed.

The relative volatility of a solvent compared to water affects the energy needed to recover the solvent using evaporators and distillation columns. We compared DMSO (b.p. 189°C) to three other high-boiling organic solvent with varying relative volatility, 1-MI (b.p. 198˚C), morpholine (b.p. 129˚C), and acetic acid (b.p. 118°C). As seen in Figure D.2, evaporators are unable to recover a high percentage of the morpholine and acetic acid. Furthermore, the number of distillation columns needed to recover products from a feed stream of 40% solvent still exceeds the feasibility limit of 5 parallel columns. This demonstrates that solvents with low relative volatility cannot be economically recovered.

Similar to the high boiling solvents, there are clear differences in separation costs for low boiling solvents. These differences are highlighted in a comparison between ethanol (b.p. 87°C) and acetone (b.p. 56˚C). As mentioned previously, distillation column constraints require a feed concentration of at least 30% ethanol which caused a gap between the product achievable with membranes and this feed concentration required by a distillation column. However, acetone is able to start at 13% feed concentration and yield

a product with 90% purity and a 0.995 solvent recovery at a cost of $2.10/kg lignin. This shows the significant impact of solvent choice and relative volatility differences. In addition to volatility considerations, ethanol has an azeotrope and acetone does not. This azeotrope would complicate distillation units attempting to reach solvent purities close to 100%. However, for the calculated scenarios in the present work, the ethanol azeotrope does not have an effect.

5.3.3.4 Reflux Ratio of Distillation Column

For the requirement of a 90% product purity and recovery, the minimum reflux ratio needed differs between high-boiling (R_{min} = 0.04) and low-boiling (R_{min} = 1) solvents. Increasing the reflux ratio increases the internal flows, which changes the flooding and weeping conditions in the column and may lead to larger column diameters. In both cases, doubling the reflux ratios result in cost changes of less than $0.02/kg lignin.

5.3.3.5 Number of Stages in Distillation Column

While there is flexibility in the number of distillation column stages, a higher number is needed for the low-boiling solvent, compared to the high-boiling solvent, due to relative volatility differences. For the two particular solvents we tested (ethanol and DMSO), the number of stages is increased by 50%. Despite these changes, the overall cost increases by less than $0.02/kg lignin.

5.3.3.6 Solvent loss in process

Although the solvent loss from the treated woodchip stream (Figure 15) is not within the scope of this study, the cost of replacing this solvent is still a line item to consider when designing an LVPP process. Our assumption of a 2% solvent loss translates to 4,700

kg/h (or 37,000 metric ton/year). With an ethanol price of $1.50/gal, an additional $0.2/kg lignin is needed to cover the cost to replenish the lost ethanol. At a price of $8.81/gal, DMSO is a more expensive solvent and an additional $1.2/kg lignin is needed to cover the cost to replenish the lost DMSO. These numbers are on the same order of magnitude as the capital and operating costs of solvent recovery, which suggests that overall solvent recovery is an important parameter for process design and optimization.

5.3.3.7 Annual interest rate

The interest rate is used to calculate annuity payments for the capital cost along with the expected lifespan of the equipment (see APPENDIX D). Doubling the interest rate from 5% to 10% increases the capital annuity payments by 50%, while reducing the interest rate to 2% cuts the capital annuity payment by 75%. However, because the operating cost of each unit considered is significantly higher than the capital cost of the units themselves, increasing the interest rate does not significantly impact the total process cost where even tripling the interest rate to 15% only raises the total cost by $0.03/kg lignin.

5.3.3.8 Lifespan of the unit

The expected lifespan of the equipment is also used to calculate capital annuity payments. Doubling the lifespan from 20 years to 40 years decreases the annuity payments in half, while reducing it to 10 years increases the payments by 60%. Extending the expected lifespan does not significantly change the total process cost, where reducing the lifespan to 10 years only increases total cost by $0.02/kg lignin.

5.3.3.9 Solvent Concentration in Feed

Keeping the solvent flow rate constant at 233,333 kg/hr, the water flow rate can be varied to change the solvent concentration in the feed. For this analysis, the separation method used is an evaporator-distillation column combination. The evaporator concentrates the solvent to 40%, and the distillation column raises the concentration to 70%. Reducing the feed concentration from 10% solvent to 5% solvent increases the total process cost from $1.10/kg lignin to $1.40/kg lignin, while increasing the feed concentration to 15% cuts the cost down to $0.80/kg lignin. Out of all the factors we have investigated, feed concentration is the most significant factor because it affects both the capital and operating costs of the process.

5.3.4 Alternatives to water-precipitation

The possibility of directly boiling off the solvent from wood chips without first washing the chips with water was considered. With substantially less liquid to process, the cost of solvent extraction is significantly reduced. This technique would only be feasible if the boiling point of the solvent is lower than the temperature range at which lignin decomposes (200-500°C) (Brebu and Vasile 2010). The boiling point of DMSO is 189°C, a prohibitive temperature where the lignin is partially decomposed. At a lower pressure of 0.5 bar, ASPEN calculations predict the boiling point of DMSO to be below 150°C which is outside the lignin decomposition range, so it might be possible to run this process at this lower pressure. Ethanol has a normal boiling point of 78°C, and there is precedence for boiling off the solvent and skipping the water dilution and precipitation (Muurinen 2000). Exploration of these scenarios is outside the scope of this chapter but are highly relevant to future LVPP implementation.

5.4 Conclusions

This work presents techno-economic models of separation methods for an LVPP process with water precipitation. A current market value of lignin is $250 - $500/ton (de Assis, Greca et al. 2018). This value is lower than the cost for any of the methods presented for both the 70% and 90% target solvent concentrations. Given these values, a solvent recovery process that starts at 10% solvent will require the development of new separation techniques that can operate within a wider range of solvent concentrations, or a higher lignin selling price to be economical. The starting solvent concentration also significantly affects the process cost, so starting the process at higher solvent concentrations may make it more economically feasible. This work highlights the distinct challenges associated with water-precipitation of a high-volume solvent stream. The typical flow rate in an industrial brownstock washing process is around 700,000 kg/hr, which is almost 3x lower than the total flow rate in our process.

For LVPP, alternative precipitation techniques are required given current lignin selling prices and typical flow rates in similar processes used in industry. The problems faced in this system are similar to those faced in any system with dilute separation targets in large quantities of water (e.g. biological production of pharmaceuticals and chemicals at low titers). Given the current state of industrial separations, alternative process operations should be explored to meet the aforementioned specifications. Finally, as most LVPP solvents are high-boiling, water addition to the process should be minimized to reduce the amount of energy required to boil the water away from the process.

CHAPTER 6. SOLVENT SCREENING FOR LVPP

6.1 Introduction

As described in CHAPTER 1, chemical pretreatments are the broadest and most prevalent strategy to convert biomass into products. These pretreatments are relevant across multiple industries from pulp and paper to biofuels to materials. Pulp and paper settled on the Kraft process utilizing sodium hydroxide (NaOH) and sodium sulfide (Na_2S) but has explored alternatives such as amine, alcohol, and glycol pulping (Johansson, Aaltonen et al. 1987). The biofuels industry began with dilute acid but has expanded into ionic liquids, deep eutectic solvents, and a multitude of individual organic solvents (Kumar, Barrett et al. 2009). The chemicals and materials industry has focused mainly on simple organic solvents, such as methanol or acetone (Baker and Rials 2013). Representing blossoming industries, early design concepts for biofuels and materials focused on an effective chemical pretreatment and subsequent optimization. Review articles have enabled comparison of treatments (Shuai and Luterbacher 2016), and new screens are being developed to select a pretreatment from a large library of chemicals (Mellmer, Sanpitakseree et al. 2018).

Screening of chemical pretreatments for pulping, fuels, and materials require different criteria due to different products and technical readiness levels. For pulp, a chemical's impact on yield and quality of the cellulose fiber reign supreme (Rodríguez, Espinosa et al. 2018). In contrast, biofuel production tracks the substrate and impacts various substrate properties, such as lignocellulosic accessibility, crystallinity, degree of polymerization, processivity, hydrolysability, product inhibition, jamming, clogging, and

reactivity (Mansfield, Mooney et al. 1999, Bansal, Hall et al. 2009). Furthermore, the production of renewable chemicals and materials focuses on the production of broken-down sugars and lignin (Shuai and Luterbacher 2016). For LVPP, i.e. a pulping process that combines a Kraft treatment with an organic solvent treatment, a different selection methodology is required.

LVPP uses a two-step process to leverage the selective delignification of organic solvents with the effective pulp production of the Kraft process (Kwok, Luettgen et al. 2017). Lignin from organic solvents is typically less condensed and more amenable to downstream valorization than Kraft lignin (Kubo and Kadla 2004). Similarly, pulp from the Kraft process is typically stronger and brighter than organic solvent pulp, especially for softwoods (Johansson, Aaltonen et al. 1987). However, there are studies that show similar or improved pulp quality for certain applications (Muurinen 2000). In addition to improved products, the two-step process seeks to improve the throughput of a pulp mill by reducing lignin loads to the recovery boiler and decreasing bottlenecks throughout the plant (Axelsson, Olsson et al. 2006). Towards selecting an organic solvent, this work follows a methodology similar to alternatives assessments published by the Environmental Protection Agency. Figure 18 depicts the screening criteria to select preferred solvents for LVPP.

` Solvent selection is explored in all process development, but the pharmaceutical industry has become a leader in this research space. Beginning in 2005 with the American Chemical Society - Green Chemistry Institute Pharmaceutical Roundtable, a large collaboration of pharmaceutical industry leaders has worked to encourage the

implementation of greener processes, resulting in two generations of ACS Solvent Guides (ACS 2011).

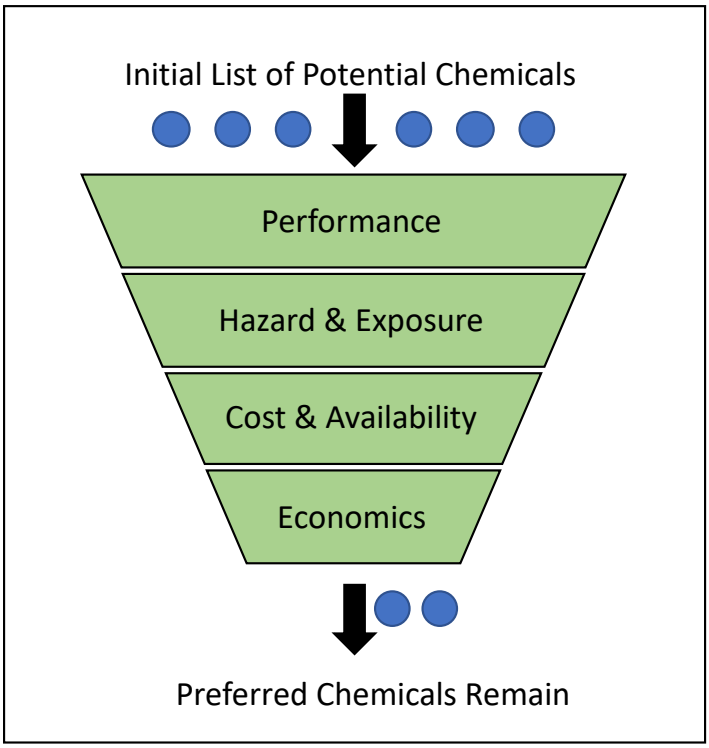


Figure 18. Alternatives assessment methodology (Adapted from (Cohen and Lewandowski 2016)).

Independently, major companies, such as GlaxoSmithKline (Henderson, Jiménez-González et al. 2011), Sanofi (Prat, Pardigon et al. 2013), and Pfizer (Alfonsi, Colberg et al. 2008), all published their selection guide criteria. The most recent work on solvents for the pharmaceutical industry is embodied in CHEM21's solvent selection guide that looked to combine and standardize the aforementioned selection guides (Prat, Hayler et al. 2014). This methodology was implemented for classical solvents, and a framework was developed for all solvents based on their physical, toxicological, ecological, and hazard characteristics (Prat, Wells et al. 2015). CHEM21 utilizes health, safety, and environmental scores that are based on Safety Data Sheet information. While these selection guides may be useful

for pharmaceutical applications, additional performance and economic criteria must be employed for a pulp mill and biorefinery. The present work takes CHEM21's scoring system to represent the hazard and exposure criteria, and it uses additional screens to dictate solvent selection for LVPP.

As discussed in SECTION 1.3.4.4, there are many individual organic solvents that have demonstrated successful fractionation of biomass for both pulping and renewable chemical production. These solvents represent just a minute fraction of the overall solvent space, but they provide valuable insight into positive solvent characteristics and the chemical moieties that enhance those characteristics.

As seen in Figure 19, we selected 30 organic solvents with similar chemical moieties and varied physical properties to highlight key screening criteria for LVPP. The solvents include alcohols (methanol, ethanol, EG, propylene glycol [PG]), ethers (tetrahydrofuran, 2-methyltetrahydrofuran, 1,4 dioxane, 2-methylfuran), esters (γ-butyrolactone [GBL], GVL, ethylene carbonate, propylene carbonate), ketones (acetone, 2-Hexanone) amines (ethylamine, 1-methyl piperazine, 2-methylpiperidine, piperidine, pyridine, pyrrolidine, N-methylpyrrolidine, HMDA), organosulfurs (DMSO, sulfolane), and multi-functional solvents (solketal, morpholine, diethanolamine, triethanolamine, N-methyl-2-pyrrolidone [NMP], isoxazole, and 1-MI). From this base group of solvents, this solvent selection methodology presents key criteria for LVPP that is applicable to any future solvent library.

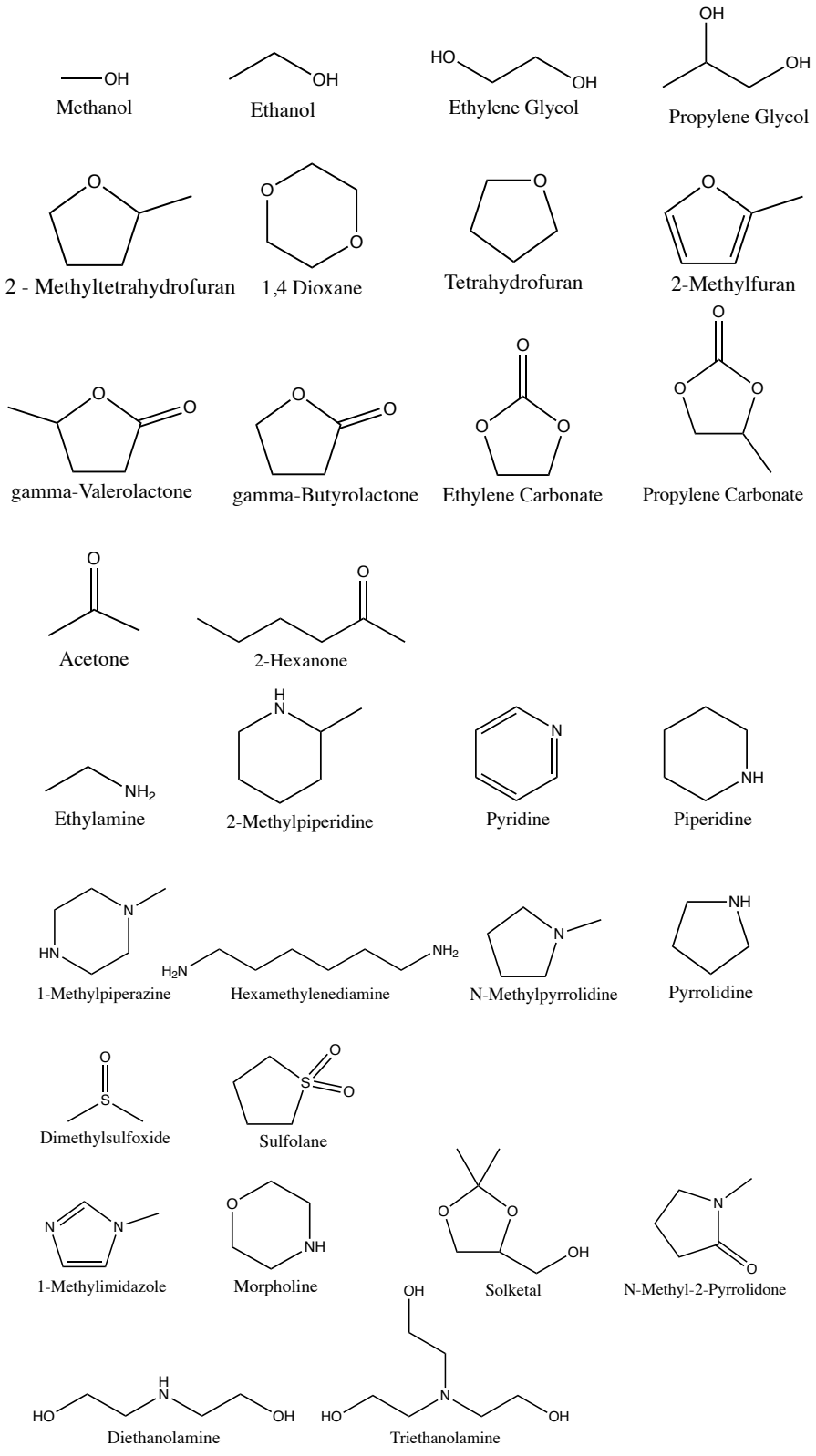


Figure 19. Organic solvents for LVPP solvent selection screen.

6.2 Materials and Methods

6.2.1 Solvents

Solketal was provided by InKemia Green Chemicals (Houston, USA), ethylene carbonate and propylene carbonate were purchased from Huntsman Corp (The Woodlands, USA), and all other organic solvents were purchased from VWR International (Radnor, USA). Sodium hydroxide, sodium sulfide, and sodium carbonate for the Kraft cook were also purchased from VWR International (Radnor, USA).

6.2.2 Substrates

Lignin samples and juvenile slash pine chips were provided by American Process Inc. (Thomaston, GA) and Georgia-Pacific (Memphis, TN) as described in SECTION 3.2.1. In short, the lignin was isolated from mixed hardwood by a mixture of sulfur dioxide, ethanol, and water at 150˚C. For lignin solubility experiments, the substrate was sieved to a size fraction of 75 µm – 150 µm and dried at 50˚C. For characterization, the lignin was sieved to a size fraction of 300 µm to 200 µm. All woodchips used in experiments were screened through 4 – 8 mm roll screens and air dried.

6.2.3 Solubility Tests

Solubility tests were performed as described in SECTION 3.2.2. In short, lignin was mixed with a 30% aqueous solution of organic solvent and allowed to reach equilibrium in a rotating mixer at 23˚C. Undissolved lignin was recovered by vacuum filtration, and solubility was determined gravimetrically

6.2.4 Treatment

Treatment was performed as recommended in SECTION 3.2.3. All pretreatments were done at 50% aqueous solution of organic solvent in a 600 mL benchtop reactor (Series 4563, Parr Instrument Company, Moline, USA). The solution was treated at 200˚C for two hours and washed in excess water. Moisture content was determined by a moisture analyzer (LJ 16, Mettler Toledo, Columbus, USA). The order of the treatments was randomized before starting.

6.2.5 Lignin Characterization

Klason lignin was determined as described in SECTION 2.2.3. A modified version of NREL's Determination of Structural Carbohydrates and Lignin in Biomass (Sluiter, Hames et al. 2008). Dry, milled samples were treated with concentrated and then dilute sulfuric acid. The precipitated, acid-insoluble lignin content was determined gravimetrically as a fraction of the initial biomass.

6.2.6 Distillation modeling

Modeling of distillation in ASPEN+ (Aspen Technology, Bedford, USA) was performed based on a model described in SECTION 5.2.2. An inlet feed of 50,000 kg of 50% aqueous solvent was distilled to a target purity of 80% aqueous solvent. The mass recovery was set at 0.995. The reflux ratio, feed stage, and distillate-to-feed ratio, and total number of stages was predicted using a DSTWU column. These initial values were then modeled with a RADFRAC process model. A unique simulation was done for each solvent to ensure proper customization of the various metrics, and a different process flowsheet was used for high key and low key solvents. Operating costs were calculated based on the steam requirements for the reboiler heat duty. Capital costs were calculated in ASPEN+ after modeling with a RADFRAC process model.

6.2.7 White Liquor Titration

White liquor titration was performed as per the TAPPI White Liquor ABC test (ELN-010.3). White liquor is diluted in water and mixed with barium chloride. This solution is titrated with 0.1N HCl to pH 9.3. After addition of formaldehyde, the solution is titrated with 0.1N HCl again to pH 9.3 and subsequently to pH 4.0.

6.2.8 Kraft Cooks and LVPP Characterization

After a 70% pretreatment step (SECTION 3.2.3), wet chips were cooked with white liquor in a 600 mL benchtop reactor (Series 4563, Parr Instrument Company, Moline, USA) with an active alkali charge of 18% per bone dry chips. Sulfidity was 20% and an H-factor of 1300 with a ramp of 2 ˚C per minute. The resulting pulp was disintegrated according to ISO 5263-1:2004 and screened. Yield was measured gravimetrically on the basis of original solids, and Kappa number was measured according to ISO 302:2004(E). Fiber properties were measured using a Fiber Quality Analyzer (FQA, OpTest Equipment Inc., Hawkesbury, Canada).

6.3 Results and Discussion

Five screening categories were assessed as outlined in Figure 18. Each category consists of one or more metrics and is calculated for all solvents within this study.

6.3.1 Performance

Three metrics were considered for the efficacy of an organic solvent in the LVPP process: (1) lignin content of residual biomass after pretreatment, (2) solubility of a technical lignin in the organic solvent, and (3) the impact of residual solvent on the white liquor of a Kraft cook. All performance screens are quick experiments that require less than

50 mL of total solvent and less than two weeks of cumulative experimental time. The conditions for both pretreatment and solubility experiments are based on recommendations from a series of experiments in CHAPTER 4. The residual organic solvent concentration of 2% for white liquor experiments is based on wood chip washing experiments.

The first performance screen is the residual acid-insoluble lignin content after a 200˚C treatment for 2 hours by a 50% v/v aqueous organic solvent mixture. Residual lignin was determined for each pretreatment as depicted in Figure 20.

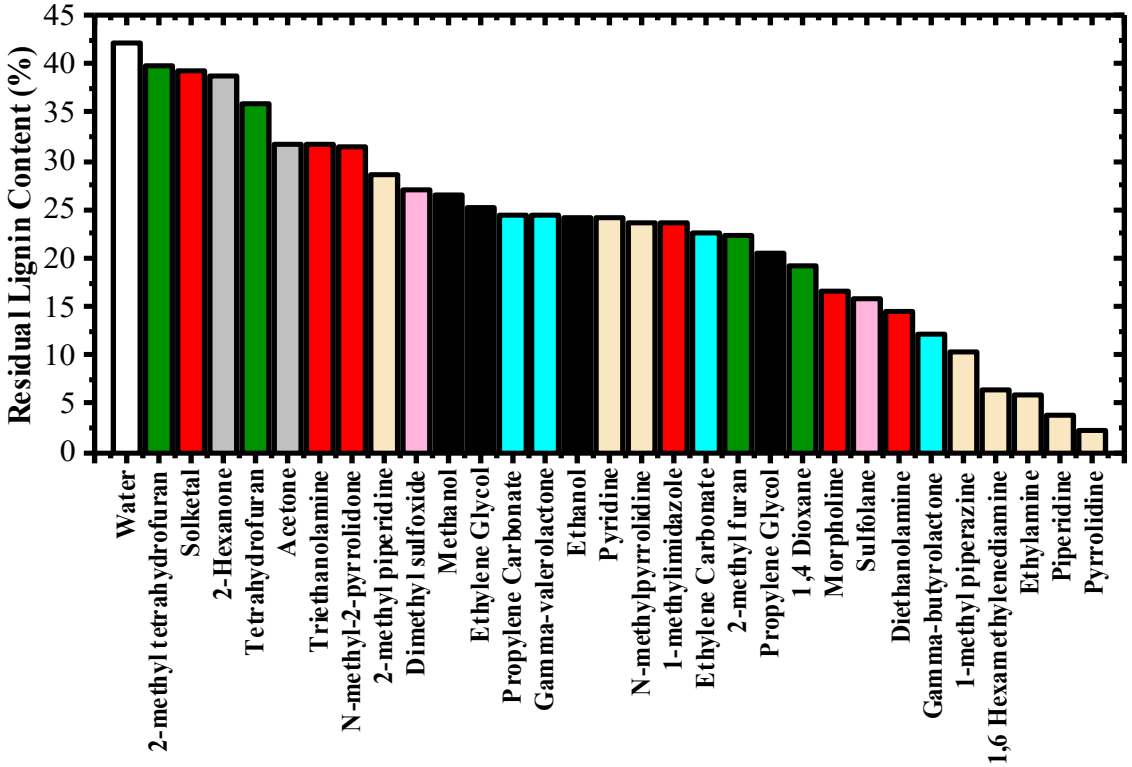


Figure 20. Residual acid insoluble lignin in biomass after pretreatment. Colored by functional group type.

With the removal of most hemicellulose during treatment, a residual lignin content of less than 20% is a significant reduction of lignin. It represents over 40% removal of

original lignin. Except for the ketones (acetone and 2-hexanone), at least one solvent from each functional grouping exhibits this significant delignification. However, the amines outperform all other groups with an average residual lignin content of 13%. This represents almost 65% removal of original lignin and signals that the necessary reduction in severity may be accomplished for these solvents. The 11 solvents that meet a cutoff criterion of 20% residual lignin content are PG, 1,4 dioxane, GBL, ethylamine, 1-methyl piperazine, piperidine, pyrrolidine, HMDA, sulfolane, morpholine, and diethanolamine.

Figure 21 compares the solubility of an industrial lignin in 30% solvent mixtures.

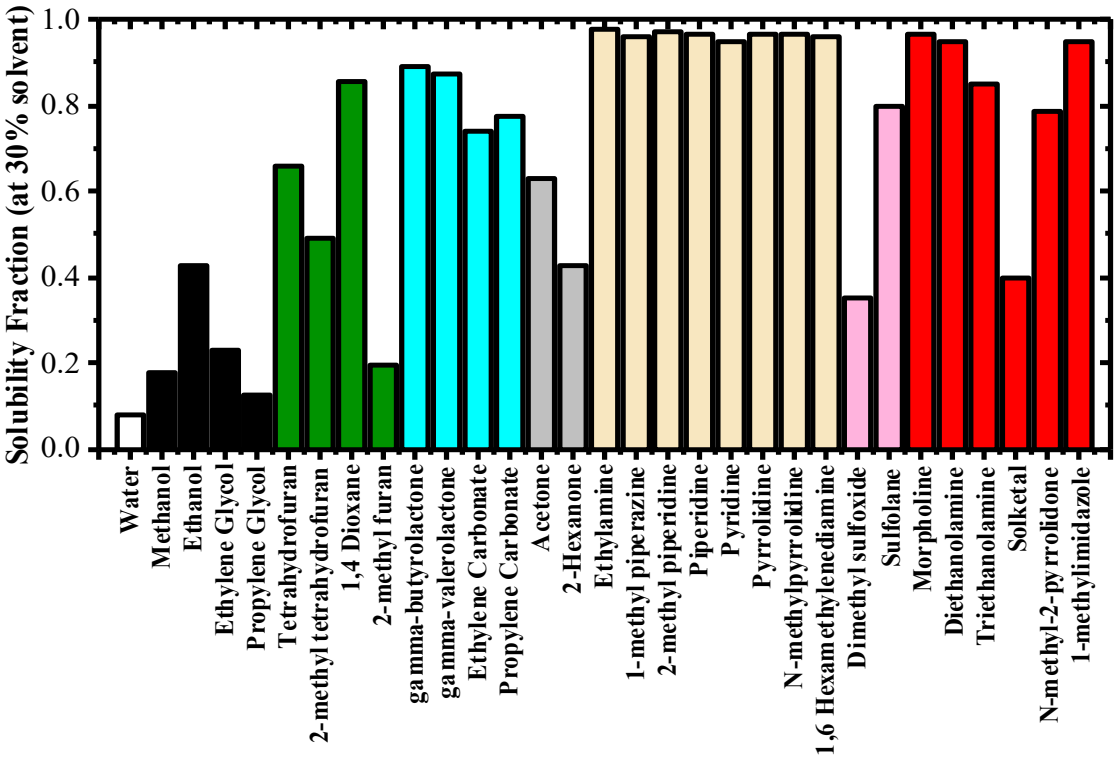


Figure 21. Solubility fraction of industrial lignin in 30% organic solvent mixtures. Colored by functional group type.

The work presented in CHAPTER 3 shows that a high solubility fraction at low solvent concentration is indicative of a broad range of solvent efficacy. Succinctly, if a

solvent has a high solubility fraction at 30%, it will maintain its high solvent loading efficacy at lower solvent loadings. Low solubility solvents, such as EG and solketal, demonstrate precipitous increases in residual lignin at lower organic solvent loadings. In EG, residual lignin increases from 21% to 39% upon decreased solvent loading from 0.70 to 0.30. In the case of solketal, residual lignin increases from 18% to 40%. By contrast, 1-MI has a much smaller increase from 23% to 28% and HMDA still reaches a residual lignin content of 15% at 0.30 organic solvent loading. We note that the amine solvents exhibit high solubility fractions along with the ester solvents. Of the 11 high performing solvents, only PG exhibits a solubility fraction less than 0.7.

A final performance metric is the impact of minimal organic solvent on the active alkali of white liquor. Only 5 solvents (NMP, GVL, GBL, propylene carbonate and ethylene carbonate) reduced the active alkali by more than 3%. The lactones and carbonates reduced the alkali by 6% and 16% respectively. The base-catalyzed hydrolysis of ester bonds renders this group of compounds unsuitable for LVPP's two-step process. Lactones and cyclic carbonates are effective at removing lignin (Zhang, Rackemann et al. 2013, Luterbacher, Rand et al. 2014), but are incompatible with the white liquor of LVPP.

6.3.2 Hazard & Exposure

The implementation of a new process requires careful consideration to the associated hazard and environmental exposure risks, as well as process chemical costs. Towards a smarter and sustainable process, we implement an extension of CHEM21's solvent selection guide for all listed chemicals. A detailed procedure for this implementation can be found in APPENDIX E. Table 26 presents the CHEM21 rankings based on a health, environment, and safety scoring system.

Table 26. Recommendations from CHEM21 Solvent Selection Guide.

Solvent	Default CHEM21 Ranking	CHEM21 Based Final Ranking
Water	1	Recommended
Methanol	2	Recommended
Ethanol	1	Recommended
Ethylene Glycol	1	Recommended
Propylene Glycol	1	Recommended
Tetrahydrofuran	2	Problematic
2-methyl tetrahydrofuran	2	Problematic
1,4 Dioxane	2	Hazardous
2-methyl Furan	3	Hazardous
γ-butyrolactone	2	Hazardous
γ-valerolactone	2	Problematic
Ethylene Carbonate	2	Problematic
Propylene Carbonate	2	Problematic
Acetone	2	Recommended
2-Hexanone	2	Hazardous
Ethylamine	3	Hazardous
1-methyl piperazine	2	Problematic
2-methyl piperidine	2	Problematic
Piperidine	2	Problematic
Pyridine	1	Hazardous
Pyrrolidine	3	Hazardous
N-methylpyrrolidine	3	Hazardous
1,6 hexamethylenediamine	2	Problematic
Dimethyl sulfoxide	1	Problematic
Sulfolane	3	Hazardous
Morpholine	2	Problematic
Diethanolamine	2	Problematic
Triethanolamine	1	Recommended
Solketal	2	Problematic
N-methyl-2-pyrrolidone	3	Hazardous
1 - Methylimidazole	2	Problematic
Solvents are grouped into functional groups: alcohol (black), ether (green), ester (blue), ketone (grey), amine (yellow), organosulfur (pink), and multi-functional (red).		

There are several differences between the CHEM21 final ranking and the CHEM21 ranking by default. The changes to methanol, acetone, 1,4 Dioxane, pyridine and DMSO were recommended changes from CHEM21 authors. The authors cite occupational exposure limits, regulatory issues, and additional information found in other solvent selection guides as guiding these changes. Along these same lines, 2-hexanone and GBL

are given hazardous scores in the present work. 2-hexanone has a low score from the International Council for Harmonisation of Technical Requirements for Pharmaceuticals for Human Use guidance for industry, and it is recommended for replacement by Sanofi's solvent selection guide (FDA 2018). GBL has been designated as a List I chemical of the controlled substance act in the United States and is therefore unsuitable for industrial use (DEA 2000).

After these changes, 1,4 dioxane, GBL, ethylamine, pyrrolidine, and sulfolane are the five high performing solvents for residual lignin that are ranked as problematic by CHEM21 analysis. From that same group, only PG is a CHEM21 recommended solvent.

6.3.3 Cost & Availability

An industrial biorefinery that processes tons of wood per hour will have an extremely large organic solvent usage. Although solvent recovery is a key consideration to minimize solvent costs, the cost and availability of a solvent is important in considering its implementation in LVPP. However, predicting solvent cost and availability comes with two distinct challenges. First, the cost databases are volatile and not publicly available for all solvents. Second, the potential cost may be dramatically lowered if there is sustained industrial demand. To address these concerns, we implement a cost and availability metric that is based on base material costs and current industrial synthesis steps.

For each solvent, we present a pricing structure based on a cost from base materials and a number of industrial synthesis steps. The base materials selected are methane, sulfur, glycerol, glucose, ammonia, ethanol, methanol, ethylene, benzene, propylene, furfural, and butadiene. The 2018 market prices for each of these chemicals is presented in Table 27. For each solvent, the stoichiometric cost based on base materials is presented in Figure 22.

Table 27. Base material costs for synthesis of solvents.

Component	$/metric ton	Industry References (see Appendix C)
Sulfur	140	Wood Mackenzie Chemicals
Natural Gas	188	Georgia Public Service Commission
Glycerol	200	ICIS
Sugar	282	New York Mercantile Exchange
Ammonia	305	Wood Mackenzie Chemicals
Ethanol	428	NASDAQ: Ethanol Futures
Methanol	430	Methanex
Ethylene	440	ICIS
Benzene	554	Wood Mackenzie Chemicals
Propylene	858	Wood Mackenzie Chemicals
Furfural	1014	CN Chemicals
Butadiene	1089	Wood Mackenzie Chemicals

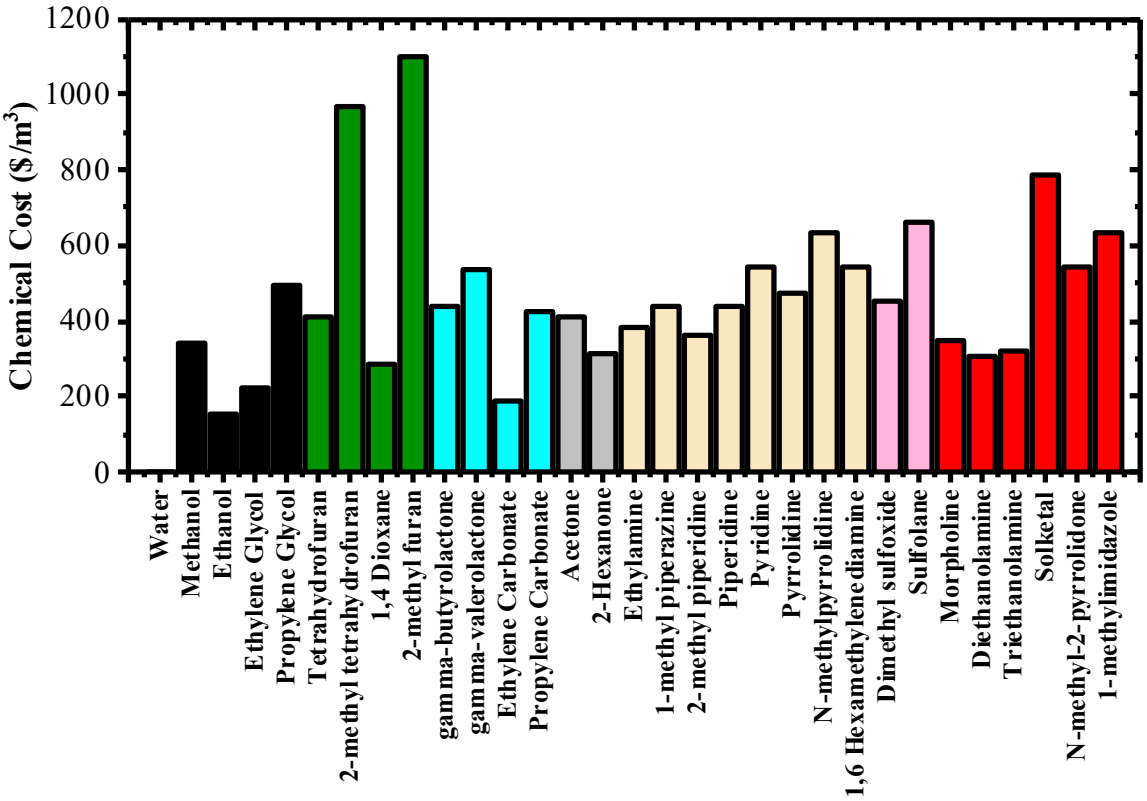


Figure 22. Chemical cost of each organic solvent based on base material costs.

An additional consideration is the number of industrial steps required to go from base material to final product. These range from 0 to 7 steps with six chemicals that take more than 4 steps (GBL, N-methylpyrrolidine, NMP, piperidine, pyrrolidine, and THF). Depending on the selected base materials, these step counts may vary. All stoichiometric reactions and steps are presented in APPENDIX E. For a reaction A + 2B = C, the stoichiometric cost of C is calculated as Equation 4,

$$C * MW_C = A * MW_A + 2 * B * MW_B. \quad (4)$$

Where A, B, and C are the cost of each chemical ($/metric ton) and MW_A, MW_B, and MW_C are the molar masses of each chemical (g/mol). In one instance, the Hock process for acetone production also yields a valuable co-product phenol. To maintain consistency while accounting for this co-product, we subtract the stoichiometric price of phenol from the stoichiometric price of acetone. Each user of this solvent selection methodology will have his/her own internal base material costs and may choose to add alternative base materials to predict cost. This methodology presents one way to compare solvents with different market sizes and different synthesis optimization levels.

For LVPP, we encourage a solvent with a calculated chemical cost of ≤$562/m^3 and an industrial synthesis route with fewer than 4 steps is encouraged. The $562/m^3 metric is selected by a simple profit upper bound (PUB) assumption for the pretreatment step. With an estimated 2% solvent loss, 4:1 liquor to wood ratio, and 40% delignification, any solvent cost ≥$562/m^3 would require ≥$250/metric ton minimum lignin selling price. Given these metrics, the cost & availability screen excludes five high performing solvents for residual lignin: GBL, 1-methyl piperazine, pyrrolidine, piperidine and sulfolane.

6.3.4 Process Economics

Since the implementation of Kraft cooks, the pulping industry has focused on recovering treatment chemicals. For all organic solvent processes, the solvent recovery process is a key economic parameter that often makes or breaks a process. Therefore, a screen on a solvent's separation efficiency may act as a process economics screen. For pulp biorefineries that are heavily tied to water, the concentration of an aqueous solvent mixture from 50% to 80% organic solvent is a useful screen. Each solvent was separated from water in a standardized ASPEN+ distillation model. The steam demand (operating cost) and annualized capital costs were combined and compared in Figure 23. Four solvents, labeled with asterisks, could not be reach an 80% purity and maintain the required solvent recovery

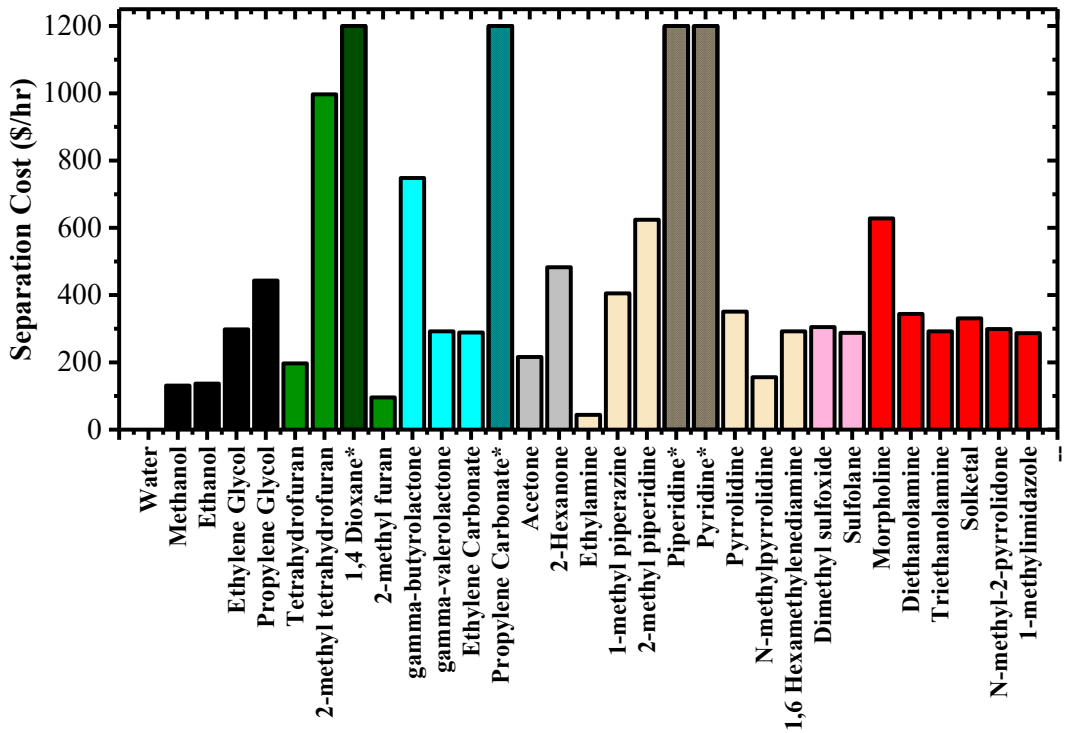


Figure 23. Comparison of separation costs (textured columns cannot be separated given purity and solvent recovery constraints).

There is clear differentiation in Figure 23 between the high performing and low performing solvents. Solvents with separation cost values ≤$500/hr are recommended. 1,4 dioxane, GBL, piperidine, and morpholine are the effective delignifying solvents that fail this screen. The other seven selected solvents are recommended by this screen.

6.3.5 Preferred Chemicals

After evaluating an initial list of 30 solvents through a delignification treatment screen, 11 organic solvents were promising candidates for LVPP. These 11 solvents were passed through 5 additional screens with different cut-offs. Table 28 demonstrates the results of each screen and shows that HMDA and diethanolamine pass all screens.

Table 28. Selection screen results for organic solvents that pass residual lignin screen.

Organic Solvent	Hazard & Exposure	White Liquor	Process Economics	Cost & Availability	Solubility
HMDA					
Diethanolamine					
Propylene Glycol					
1-methyl piperazine					
Morpholine					
Piperidine					
Ethylamine					
Pyrrolidine					
Sulfolane					
1,4 Dioxane					
γ-butyrolactone					

PG only fails the solubility screen, and 1-methyl piperazine only fails the cost and availability screen. As these two screens contain the most assumptions, we highly recommend exploring both solvents. Of the remaining solvents, morpholine only fails the process economics screen and is therefore preferred over the other solvents.

6.3.6 HMDA as a promising candidate for LVPP

After the LVPP solvent selection process, HMDA was preliminarily explored as a potential LVPP candidate solvent. In conjunction with the techno-economic analysis found in CHAPTER 4, we explored two different LVPP treatments with HMDA. In a two-step process, we selected less severe pretreatment conditions to maintain wood chip integrity for the second Kraft pulping step. A treatment of 200˚C for 30 min and a treatment 185˚C cook for 90 min were followed by a Kraft cook to a Kappa number of 60. Both treatments produced pulp yields and fiber lengths that were not significantly different from a control Kraft cook. Different from the control Kraft cook, the two streams yielded lignin streams of 12% and 13% respectively on the basis of original chip mass. This corresponds to an organic solvent delignification of approximately 40%. Based on these preliminary results, the 185˚C treatment for 90 min was used in CHAPTER 4.

6.4 Conclusions

Solvent selection guides from the pharmaceutical industry are seminal works that have pushed the field towards sustainable solvents. The present work builds on those hazard & exposure considerations and presents a solvent selection, specifically tuned for the LVPP process. Performance and economic screens are presented based on the key process indicators from CHAPTER 4.

The performance screens address the residual lignin assumption from CHAPTER 4 and are based on work from CHAPTER 3. The present work is the first side-by-side comparison of organic solvent treatments on juvenile slash pine chips under identical conditions. In addition to providing insight into LVPP, this work may be used to direct future research into any of these solvent candidates. However, one must remember from

CHAPTER 1 that the delignification efficacy on slash pine chips does not directly correlate to efficacy on other feedstocks.

The separation screen addresses the costliest unit operation in LVPP and provides a basic estimation of separation costs. As discussed in CHAPTER 5, alternative methods of separation may be utilized for solvents that cannot be adequately separated in a distillation unit. Finally, the cost estimation addresses the solvent cost. The solvent price assumption is listed in CHAPTER 4 as a minor assumption due to the low impact of 10% changes in solvent cost to the final lignin price. However, the wide range of solvent costs poses a threat to LVPP viability. We present the first methodology for costing industrial solvents based on a set of base materials. Market price adjustments and modification of base materials may lead to improved cost estimation.

In summary, this solvent selection methodology may be rapidly applied to any set of solvents for LVPP. Each selection screen provides valuable information on the potential efficacy of a solvent on LVPP, and our initial screen has resulted in four highly promising solvents. Future work will deepen our understanding of how these selected solvents perform across the LVPP process.

CHAPTER 7. RECOMMENDATIONS AND CONCLUSIONS

Unlocking a pulp mill is the most straightforward way to renewable chemicals from lignocellulosic material. Utilization of the existing capital, logistics, and industry know-how will be critical in the advancement of renewables. LVPP is a potential key to sustainably solving this challenge. Optimization of this process and a greater understanding of its mechanisms of action are highly desired.

7.1 Recommendations for future research

7.1.1 Kinetics of organic solvent pulping

Understanding the kinetics of organic solvent pulping will enable the selection of optimal treatment conditions for a given process. Kraft pulping activation energies have been calculated across different species based on experiments performed at varying severities (Almeida, Santos et al. 2015). The activation energy of lignin removal by white liquor is used to determine the H-Factor, a common quantification of digester treatment severity (Vroom 1957). A review of organic solvent pulping techniques has demonstrated different correlations between pulp yield and kappa number (Johansson, Aaltonen et al. 1987). These differences hint at changes to the activation energy of lignin removal and should be investigated. Our preliminary work on HMDA delignification of slash pine suggests an activation energy of 139 kJ/mol, which is similar to that of white liquor on pine (Almeida, Santos et al. 2015). Understanding the differences across solvents would be highly valuable to the community.

7.1.2 Vacuum washing of wood chips

As presented in CHAPTER 4, the viability of LVPP hinges on an effective solvent removal from wood chips between treatments of organic solvent and white liquor. Chip washing apparatuses have been patented by Valmet and are frequently utilized in pulp mills (Kajzer and Bowie 2007). However, both experimental and theoretical work could improve our understanding of solvent removal from these large, porous materials. The penetration of solvents, mainly water, have been studied extensively and presented with governing diffusion equations (Woods 1956, Stone and Green 1958). Additional work has focused on modelling the ionic, alkali impregnation of wood (Malkov, Tikka et al. 2001, Inalbon, Mussati et al. 2011). In the former work, water has replaced air in the chips. In the latter work, the alkali has diffused throughout the water. Washing models that build on this foundation will enable an understanding of the required time and washing volume for high solvent recovery.

An alternative solution to complete removal of solvent from wood chips is by finding a solvent that is unaffected by the downstream pulping process and recoverable in the chemical recycling process. It is recommended to explore the possibility of separating the treatment solvent during multi-effect evaporation or in the recovery boiler. Thermal, aqueous, and base-catalysed decomposition studies should be performed to predict the solvent losses during a second treatment.

7.1.3 One-step process for LVPP

Another way to address the mass transfer difficulties of solvent recovery from wood chips is to explore a one-step process with a highly effective organic solvent. While organic solvent pulps have typically been weaker than Kraft cooks, a deeper look may be warranted (Rodríguez and Jiménez 2008). The solvent selection work presented in CHAPTER 6

highlights a set of 30 organic solvents, many of which have not been fully explored in a pulping environment. Developing a screen for potential fiber properties would position LVPP to transition to a process that generates lignin value during pulping. Many economic benefits are realized in a one-step process. Compared to the process described in CHAPTER 4, no new digester would be required, solvent recovery in the brown-stock washers would be possible due to a fully fibrous material, and water usage would be reduced enabling lower energy costs during solvent concentration. The one-step process hinges on quality pulp production, but it is also dependant on realized value from the isolated lignin stream.

7.1.4 CO_2 precipitation of lignin

As presented in CHAPTER 5, water precipitation of lignin is economically infeasible for LVPP. As discussed in SECTION 4.2.3, CO_2 precipitation is a technologically ready solution that should be explored for all potential LVPP solvents. As described in LignoBoost processes, CO_2 is effective at reducing pH to levels that precipitate lignin from solution (Tomani 2010). To be effective in an LVPP scenario, the CO_2 needs to have similar precipitation effects and low impact on the treatment solvent. In the LignoBoost process, NaOH reacts with CO_2 to form carbonates, but these carbonates are recycled in the green liquor cycle of a pulp mill. CO_2 precipitation experiments are critical in the next stage of LVPP process development, and an understanding of how each solvent reacts with CO_2 will impact the overall economics of the system.

As described in SECTION 4.2.3, carbon capture research by organic solvents is an important resource in solvent recovery. Reversible reactions, such as carbamate formation, would enable CO_2 sequestration and full solvent recovery. As a late-stage study, flue gas

from the downstream pulping process could be used as a CO_2 source and would provide large environmental benefits to the process. Utilizing flue gas from the lime kiln has been proposed in the LignoFuel R&D programme for the second-generation LignoBoost process (Tomani, Axegård et al. 2011).

7.1.5 Lignin characterization

Lignin characterization is frequently linked to usefulness in downstream applications. These characterizations may be studied independently or together to fully evaluate lignin samples. Technical lignin samples have been compared by several research groups (Constant, Wienk et al. 2016, Hu, Du et al. 2016). The main techniques used for analysis are CHNOS elemental analysis, GPC, 2D-HSQC-NMR, ^{13}C-NMR, ^{31}P-NMR, and ATR-IR. Together, these analytical techniques provide insight into the molecular weight, chemical composition, and the prevalence of easily broken ether bonds. Lignin characteristics vary across different treatments. Further analysis of extracted lignin will enable LVPP to target a specific lignin product and could result in a secondary performance screen.

7.1.6 Expanded Solvent Selection

As LVPP is developed, additional performance screens can be added to refine expanded solvent lists. The selection methodology presented in CHAPTER 6 utilizes our current understanding of the process. As described in this chapter, lignin and pulp quality screens could be added along with thermal decomposition screens suggested in SECTION 7.1.3. New types of solvents, including ionic liquids, could be explored from the wide range of chemical pretreatment options that were presented in SECTION 1.3.4. Further trials and more solvents will provide valuable data for future LVPP implementation.

7.2 Conclusions

7.2.1 Molecular probe – a tool to screen for pretreatment efficacy on SEB

Cellulosic accessibility is an important measure of pretreatment efficacy on biomass. The use of azo-stilbene dyes was first implemented by the pulp and paper industry (Simons 1950), and their use was investigated for preliminary LVPP solvent exploration. CHAPTER 2 outlines the development of a molecular probe, DY11, as a direct replacement for DO15 in a modified Simons' stain assay. We demonstrate that DY11 performs as well as DO15 in all tests, and significantly better in both a combined DY11-DB1 assay and on lignocellulosic biomass. Specifically, DY11 has linear absorbance extinction coefficients and a higher correlation with two-hour lignocellulosic conversion.

DY11 is a quick screen that correlates to the digestibility of treated screens. No correlation was found between delignification and DY11 adsorption suggesting solvent impacts go beyond simple solubilization of lignin. This understanding is critical to LVPP development and is a useful reminder that delignification must be paired with fiber optimization. This work on DY11 accessibility also exposes the need for specific experiments on the proposed biomass feedstocks. No correlation was found between the solvent delignification of SEB and slash pine chips.

7.2.2 Solubility vs. Delignification – predicting pretreatment efficacy for LVPP

Predicting delignification efficacy of solvents is an unsolved challenge that has pushed biomass research closer to guess-and-check rather than rational design. CHAPTER 3 explores five solvent treatments on slash pine chips and tests the hypothesis that solubility of a common industrial lignin in a solvent can predict delignification efficacy.

This study demonstrates that solubility cannot predict the extent of delignification of slash pine chips. In the process of disproving this hypothesis, this work uncovers two key results that are essential for efficient solvent selection for LVPP. First, the importance of significant water and solvent presence for treatment efficacy: 10% and 90% solvent mixtures had no efficacy on slash pine delignification. This finding, along with the large amount of water in pre-steamed chips, render 50% solvent mixtures the best screen for pretreatment efficacy. Second, lignin solubility profiles are highly varied, and solubility of industrial lignin in 30% solvent may predict the robustness of an organic solvent treatment. EG, with its low 30% solubility, has a large delignification efficacy drop when its solvent loading is decreased. In contrast, 1-MI and HMDA have much higher 30% solubility and exhibit much smaller decreases in delignification efficacy. Additional experimentation on solketal, another low 30% solubility solvent, shows a delignification efficacy decrease from over 40% to less than 5% when its solvent loading goes from 70% to 50%. Further experimentation to understand these precipitous declines, including tests on side reactions with acetal groups, would provide mechanistic insight into the correlation between 30% lignin solubility and a robust treatment.

A final conclusion from CHAPTER 3 comes from the variation in solubility profiles across different organic solvents. These solubility disparities may be tuned for downstream lignin valorization. Whether in extracting, solubilizing, or fractionating lignin, these solvent profiles can be combined with analytical methods to explore the conversion of LVPP's lignin into valuable materials and chemicals.

7.2.3 Process Design – evaluating key unit operations for LVPP

To produce a valuable lignin stream and create a strong pulp product, LVPP

combines selective delignification of organic solvents with the high-quality pulp production of the Kraft process. Designed as an addition to a current pulp mill operation, CHAPTER 4 presents a preliminary sketch of the unit operations present in an LVPP process. This process flow sheet, along with a corresponding techno-economic analysis, lists the remaining assumptions required to model the process. The importance of each process assumption is quantified in a sensitivity analysis to direct future research. This work highlights the importance of the chip washing, carbamate CO_2 capture, and precipitation assumptions. It also highlights the current lignin selling prediction of $829/ metric ton of lignin.

Although solvent loss is a major concern, the energy required to regenerate the solvent from water is the main economic driver for LVPP's high lignin price. We outline the relatively low capital costs/per kg of lignin, and we break down the high operating costs to provide an initial perspective on LVPP's economics. This work acts as an economic tool that may be tuned to individual solvent treatments with the same process configuration. As additional process detail is elucidated, the governing assumptions will narrow to enable a more accurate lignin selling price.

7.2.4 Water Precipitation – evaluating solvent separation for LVPP

To address the unit operations that act as the main economic drivers of LVPP, CHAPTER 5 presents a comparative evaluation of separation techniques for solvent recovery from an aqueous mixture. Specifically, this chapter evaluates a proposed precipitation mechanism that involves solvent dilution by water to a final concentration of 10% solvent. We present a techno-economic model that concentrates a 10% solvent mixture, and we evaluate the required lignin selling price for separation configurations that

combine multi-effect evaporators, reverse osmosis membranes, and distillation unit operations. The separation impact of water precipitation on lignin selling price is prohibitively high, and we recommend alternative precipitation techniques. Our evaluation shows the flowrate and concentration limitations of each unit operation, and we highlight the distinct challenges associated with high-volume solvent streams.

This work explores the separation of both a low boiling solvent and a high boiling solvent. For low boiling solvents, the limitations of solvent recovery in evaporators and distillation sizing prevents solvent recovery at high flowrates (>200,000 kg/hr of solvent). With lower flowrates, the cost of solvent recovery reaches $3.00/kg of lignin and not economically viable. Direct evaporation of low-boiling solvents for lignin precipitation is recommended. For high boiling solvents and water precipitation, the best recovery cost is about $1.50/kg of lignin. This separation cost is much better than that for low-boiling solvents, but it is still not economically viable. By diluting the solvent 5-fold to reach a 10% solvent concentration, water precipitation adds high volumes of water that it must then boil off. It is clear that water precipitation is only valuable at lab scale for lignin characterization, but alternative methods of precipitation are required for LVPP.

7.2.5 Solvent Screen – a tool to screen and evaluate solvents for LVPP

Combining the results from CHAPTER 2-5, CHAPTER 6 presents a solvent selection methodology for LVPP. Using an alternatives assessment model, we evaluated a set of 30 solvents on their performance, hazards, toxicity, economics, and availability. As a new solvent selection guide, this methodology may be used specifically for LVPP without modification or may be expanded into the renewable industry with additional performance screens.

Three performance screens are considered for LVPP, a 50% solvent treatment, a 30% solvent solubility experiment, and a white liquor titration. We calculated hazard and exposure predictions with a CHEM21 methodology, determined cost estimations based on industrial synthesis steps, and modeled a distillation separation in ASPEN+ for each solvent. Given an initial set of solvents, HMDA and diethanolamine pass all screens and are designated for further exploration. PG and 1-methyl piperazine are also highly recommended by this methodology. Morpholine is the final solvent that can be recommended by this solvent selection methodology.

CHAPTER 4 and CHAPTER 6 highlight preliminary exploration of HMDA treatment as the preferred solvent for LVPP. This work is a foundation for future LVPP process development, and it demonstrates a clear opportunity to fully utilize lignocellulosic biomass for a sustainable future.

APPENDIX A. SUPPLEMENTAL MATERIAL FOR CHAPTER 2

A.1 Steam exploded treatments for DY11 experiments

The following tables present the solvents used in DY11 experiments and their respective data after solvent treatment on SEB. The data in Table A.1. was performed in duplicate and do not have error bars.

Table A.1. List of solvents and the raw data for Figure 7.

Solvent	% Conversion	Bound Dye [mg/g]	% Delignification
1-methylimidazole	56.07	62.41	64.64
2-hexanone	29.17	25.14	45.97
2-methylpiperidine	43.88	50.80	66.19
Acetone	33.26	28.96	41.95
Cyclopentanol	33.70	34.06	30.80
Diethanolamine	40.60	43.04	59.70
Dimethyl sulfoxide	45.91	51.06	57.86
Ethanol	27.22	27.20	41.73
Ethylene Carbonate	33.99	30.99	67.75
N-methylpyrrolidine	40.52	43.34	62.68
N-methyl-2-pyrrolidone	38.55	41.80	61.00
Piperidine	46.10	54.81	65.65
Pyrrolidine	58.53	70.76	73.01
Sulfolane	36.27	38.07	48.86
Tetrahydrofuran	34.88	22.71	49.15
Triethylamine	41.61	47.26	62.05
Water	34.54	25.00	18.64
γ-butyrolactone	33.69	29.98	58.92
γ-valerolactone	34.81	29.58	52.93

Table A.2. presents the raw data for Figure 8. As in the previous table, delignification of SEB is the average of duplicate experiments. The wood chip, residual lignin data was the result of single experiments.

Table A.2. Delignification data for organic solvent treatment of wood chips and SEB.

Solvent	% Delignification (SEB)	% Residual Lignin (Chips)
1-methyl piperazine	52.38	10.31
1-methylimidazole	64.64	23.60
2-hexanone	45.97	38.69
2-methylpiperidine	66.19	28.51
2-methylfuran	26.22	22.25
Acetone	41.95	31.78
Diethanolamine	59.70	14.52
Dimethyl sulfoxide	57.86	27.13
Ethanol	41.73	24.30
Ethylamine	67.60	5.97
Ethylene Carbonate	67.75	22.50
Morpholine	56.30	16.59
N-methyl-2-pyrrolidone	61.00	31.52
Piperidine	65.65	3.91
Propylene Carbonate	55.97	24.53
Pyridine	57.41	24.15
Pyrrolidine	73.01	2.17
Sulfolane	48.86	15.77
Tetrahydrofuran	49.15	35.90
Triethanolamine	48.31	31.63
Water	18.64	42.10
γ-butyrolactone	58.92	12.15
γ-valerolactone	52.93	24.38

Table A.3. Compositional analysis of SEB.

SEB Component	Composition [%]
Glucan	55.38
Xylan	0.82
Galactan	0.00
Arabinan	0.00
Mannan	0.00
Acid-soluble Lignin	2.55
Acid-insoluble Lignin	28.73
Lignin ash	3.82
Acetate content	0.33
Total determined compounds	91.63

Table A.4. Compositional analysis of SELP.

SELP Component	Composition [%]
Glucan	47.62
Xylan	0.46
Galactan	0.00
Arabinan	0.00
Mannan	0.00
Acid-insoluble Lignin	49.99
Total determined compounds	98.07

A.2 Procedure for a Modified Simons' Staining Protocol w/ DY11

Dye Fractionation:

1. Weigh out solid DY11
2. Dilute to 10 g/L with DI water
3. Syringe filter with a polyethersulfone, 0.45 µm filter
4. Syringe filter with a polyethersulfone 0.2 µm filter
5. Spin in a 50 mL polyethersulfone 100 kDa filter at 3000 x g for 30 minutes
6. Dilute retentate 2x with DI water and spin as in step 5
7. Dilute retentate 2x with DI water and spin as in step 5 (retentate is HMW DY11)
8. Combine all flow-through from steps 5-7
9. Spin flow-through in a 50 mL polyethersulfone 10 kDa filter at 3000 x g for 30 minutes.
10. Dilute retentate 2x with DI water and spin as in step 9.
11. Dilute retentate 2x with DI water and spin as in step 9. (retentate is MMW DY11)
12. Dry1000 µL of steps 7 and 11 in 60˚C oven – weigh to determine final concentration
13. Dilute HMW to appropriate working concentration (we chose 3.33 mg/mL)

Simons' Staining Method

1. Weigh 10 mg of cellulosic sample into a 2.0 mL round bottom eppendorf tube.
2. Add 100 µL of phosphate buffer (140 mM NaCl, 0.3M Phosphate, pH 6.0)
3. Add specified amount of water: 100 – 900 µL
4. Add specified amount of dye: Final Concentration Dependent
5. Close and shake tube for 6 hours at 70˚C and 500-600 rpm.
6. Dilute dye with DI water to appropriate range for spectrophotometer
7. Measure free dye concentration and then determine bound dye concentration by subtraction.

APPENDIX B. SUPPLEMENTAL MATERIAL FOR CHAPTER 3

B.1 Solubility study for juvenile slash pine chips

The experimental data presented in Table B.1 compares solubility fraction and delignification efficacy for aqueous organic solvent mixtures.

Table B.1. Delignification and solubility fraction. Standard deviation as applicable.

Solvent	Vol% Solvent	Delignification	Solubility Fraction
1-MI	10	17%	0.78 ± .02
1-MI	30	46%	0.95 ± .01
1-MI	50	57%	0.95 ± .01
1-MI	70	54%	0.95 ± .01
1-MI	90	28% ± 2%	0.96 ± .01
EG	10	10%	0.18 ± .02
EG	30	19%	0.22 ± .05
EG	50	52 ± 10%	0.35 ± .06
EG	70	58% ± 3%	0.49 ± .01
EG	90	27%	0.82 ± .01
EtOH	10	9% ± 2%	0.34 ± .06
EtOH	30	15%	0.50 ± .03
EtOH	50	56%	0.70 ± .02
EtOH	70	48%	0.85 ± .01
EtOH	90	28%	0.66 ± .02
HMDA	10	<20%[a]	0.95 ± .01
HMDA	30	69%	0.95 ± .02
HMDA	50	87%	0.92 ± .01
HMDA	70	88% ± 3%	0.93 ± .02
THF	10	11%	0.36 ± .02
THF	30	4% ± 2%	0.77 ± .11
THF	50	31%	0.93 ± .02
THF	70	70%	0.94 ± .01
THF	90	11%	0.90 ± .04

[a] *Unable to complete mass balance for delignification by HMDA 10% solvent fraction*

B.2 Lignin Characterization

The following figures and tables present a characterization of the lignin used in solubility experiments. A variety of techniques are used, and solubility should be reproducible across similar lignin samples.

Figure B.1. Gel Permeation Chromatography of American Process Lignin.

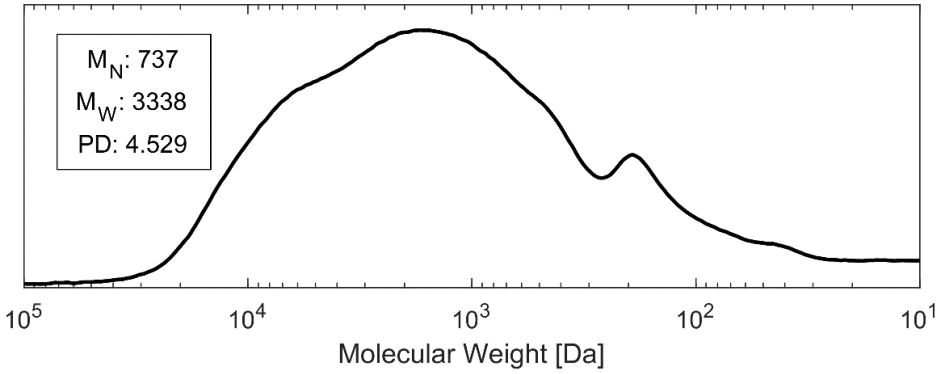


Figure B.2. 2D - HSQC NMR of American Process Lignin.

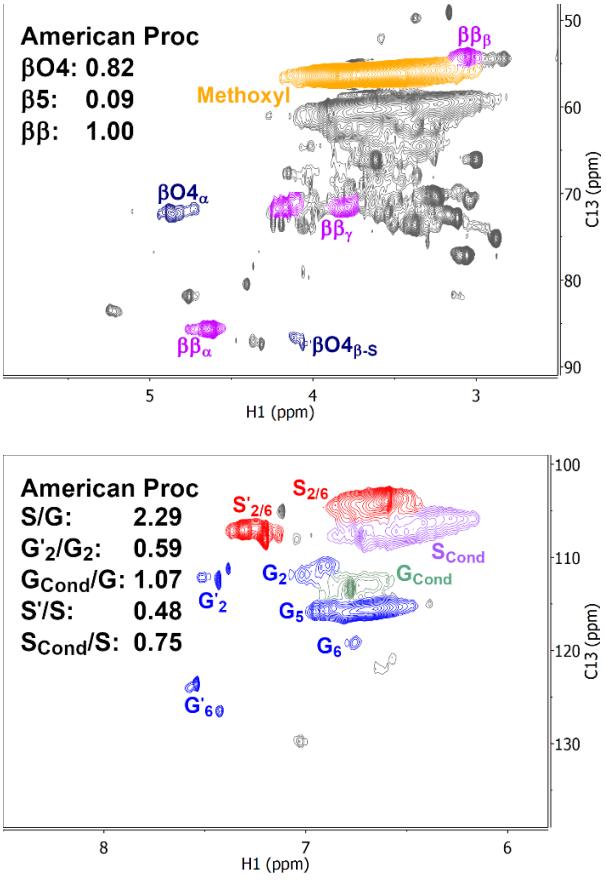


Figure B.3. Quantitative ^{31}P NMR of American Process Lignin.

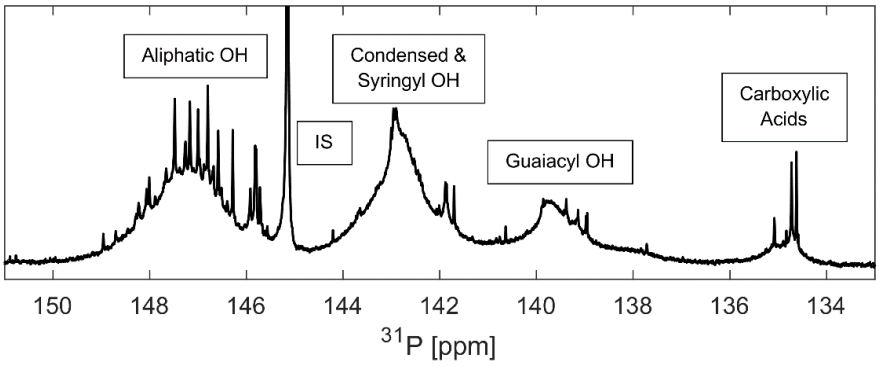


Table B.2. Quantitative ^{31}P NMR of American Process Lignin.

	Aliphatic OH	Condensed & Syringyl OH	Guaiacyl OH	Carboxylic Acids
Concentration [mmol/g]	1.72	1.67	0.689	0.156

Table B.3. Sugar Analysis of American Process Lignin.

	Arabinan	**Galactan**	**Glucan**	**Xylan**	**Mannan**
wt %	0.0	0.0	2.3	1.8	0.0

Table B.4. CHNOS analysis of American Process Lignin.

C [wt%]	**H [wt%]**	**N [wt%]**	**O [wt%]**	**S [wt%]**
57.6	5.39	0.35	33.8	2.13

Table B.5. PIXE analysis of American Process Lignin.

	PIXE (Vroom)
Na	670.3
Mg	251.3
Al	98.2
Si	156
P	0
Cl	0
K	507.9
Ca	959.5
Ti	0
Cr	119.7
Mn	65.5
Fe	967.1
Co	0
Ni	114.3
Cu	50.6
Zn	46.9
W	0
Se	0
Sr	8.1
Mo	48.7
Br	0
Nb	0

APPENDIX C. SUPPLEMENTAL MATERIAL FOR CHAPTER 4

Table C.1. Stream tables for scenario presented in SECTION 4.4.

All flows in kg/hr	Stream 1	Stream 2	Make-up	Stream 3 (s)	Stream 3 (l)	Wash 1	Stream 4 (s)	Stream 4 (l)
Temp [˚C]	25	125	125	185	185	70	70	70
Water	125000	166328	0	165323	84677	104101	301473	288202
Solvent	0	0	3499	138871	71129	0	2722	137190
Cellulose	52500	52500	0	49207	0	0	49207	0
Hexoses	17500	17500	0	13718	0	0	13718	0
Pentoses	10000	10000	0	9330	0	0	9330	0
Lignin	41250	41250	0	21296	0	0	21296	0
Extractives	2500	2500	0	125	0	0	125	0
Acetyl	1250	1250	0	625	0	0	625	0
Total Solids	125000	125000	0	94300	0	0	94300	0
Dissolved Cellulose	0	0	0	2177	1115	0	43	2135
Dissolved Hexoses	0	0	0	2501	1281	0	49	2452
Dissolved Pentoses	0	0	0	443	227	0	9	435
Dissolved Lignin	0	0	0	13196	6759	0	259	12937
Dissolved Extractives	0	0	0	1571	804	0	31	1540
Dissolved Acetyl	0	0	0	413	212	0	8	405
Dissolved Carbamate	0	0	0	0	0	0	0	0
Total Dissolved Solids	0	0	0	20301	10398	0	398	19904
CO_2	0	0	0	0	0	0	0	0
Total Flow	250000	291328	3499	418795	166204	104101	398893	445295
Next Stream	To Stream 2	Stream 3	Stream 3	Stream 4	Stream 5	Stream 4	Pulp Mill	Stream 5

Table C.2. Stream tables for scenario presented in SECTION 4.4 - 2.

All flows in kg/hr	Precipitation	Stream 5 (s)	Stream 5 (l)	Wash 2	Stream 6 (s)	Stream 6 (l)
Temp [˚C]	70	70	70	70	70	70
Water	0	11625	361253	36240	17812	30054
Solvent	0	6170	191746	0	309	5862
Cellulose	0	0	0	0	0	0
Hexoses	0	0	0	0	0	0
Pentoses	0	0	0	0	0	0
Lignin	0	18120	0	0	18120	0
Extractives	0	0	0	0	0	0
Acetyl	0	0	0	0	0	0
Total Solids	0	18120	0	0	18120	0
Dissolved Cellulose	0	101	3149	0	5.1	96
Dissolved Hexoses	0	116	3617	0	5.8	111
Dissolved Pentoses	0	21	641	0	1	20
Dissolved Lignin	0	49	1527	0	2.5	47
Dissolved Extractives	0	73	2271	0	3.7	69
Dissolved Acetyl	0	19	598	0	1	18
Dissolved Carbamate	0	447	13893	0	22.4	425
Total Dissolved Solids	0	827	25695	0	41.3	786
CO_2	3939	0	0	0	0	0
Total Flow	3939	36742	578694	36240	36282	36701
Next Stream	To Stream 5	To Stream 6	To Stream 7	To Stream 6	PRODUCT	To Stream 6

Table C.3. Stream tables for scenario presented in SECTION 4.4 - 3.

All flows in kg/hr	Stream 7 (s)	Stream 7 (bot)	Stream 7 (top)	Wash 3	Stream 8 (s)	Stream 8 (l)
Temp [˚C]	115	115	101	70	70	70
Water	3109	67948	320251	24325	11710	15724
Solvent	9054	197899	1040	0	453	8601
Cellulose	0	0	0	0	0	0
Hexoses	0	0	0	0	0	0
Pentoses	0	0	0	0	0	0
Lignin	0	0	0	0	0	0
Extractives	0	0	0	0	0	0
Acetyl	0	0	0	0	0	0
Total Solids	12163	0	0	0	12163	0
Dissolved Cellulose	0	0	0	0	0	0
Dissolved Hexoses	0	0	0	0	0	0
Dissolved Pentoses	0	0	0	0	0	0
Dissolved Lignin	0	0	0	0	0	0
Dissolved Extractives	0	0	0	0	0	0
Dissolved Acetyl	0	0	0	0	0	0
Dissolved Carbamate	0	0	0	0	0	0
Total Dissolved Solids	0	0	0	0	0	0
CO_2	0	0	3933	0	0	0
Total Flow	24326	265847	325224	24325	24326	36701
Next Stream	To Stream 8	To Stream 3	To Stream 4	To Stream 8	To Boiler	To Stream 3

Table C.4. LVPP accounting for minimum lignin selling price.

LVPP Cash	Capital Costs	15% of Capital	10-year Depreciation	Make-up Chemicals	Steam & Electricity	Lost Lignin Energy	Lignin ($829/ton)	25% Tax Rate	Earnings & Depreciation	25% IRR
Year	8.43E+07	**Maintenance**	**Depreciation**	**Feedstock**	**Energy**	**Product Loss**	**Revenue**	**Net Earnings**	**Cash Flow**	**Discounted Flow**
1		-6.32E+05	8.43E+06	-2.54E+07	-4.6E+07	-1.21E+07	1.04E+08	8.83E+06	-6.70E+07	-6.70E+07
2		-6.32E+05	8.43E+06	-2.54E+07	-4.6E+07	-1.21E+07	1.04E+08	8.83E+06	1.73E+07	1.38E+07
3		-6.32E+05	8.43E+06	-2.54E+07	-4.6E+07	-1.21E+07	1.04E+08	8.83E+06	1.73E+07	1.10E+07
4		-6.32E+05	8.43E+06	-2.54E+07	-4.6E+07	-1.21E+07	1.04E+08	8.83E+06	1.73E+07	8.84E+06
5		-6.32E+05	8.43E+06	-2.54E+07	-4.6E+07	-1.21E+07	1.04E+08	8.83E+06	1.73E+07	7.07E+06
6		-6.32E+05	8.43E+06	-2.54E+07	-4.6E+07	-1.21E+07	1.04E+08	8.83E+06	1.73E+07	5.66E+06
7		-6.32E+05	8.43E+06	-2.54E+07	-4.6E+07	-1.21E+07	1.04E+08	8.83E+06	1.73E+07	4.52E+06
8		-6.32E+05	8.43E+06	-2.54E+07	-4.6E+07	-1.21E+07	1.04E+08	8.83E+06	1.73E+07	3.62E+06
9		-6.32E+05	8.43E+06	-2.54E+07	-4.6E+07	-1.21E+07	1.04E+08	8.83E+06	1.73E+07	2.90E+06
10		-6.32E+05	8.43E+06	-2.54E+07	-4.6E+07	-1.21E+07	1.04E+08	8.83E+06	1.73E+07	2.32E+06
11		-6.32E+05	0.00E+00	-2.54E+07	-4.6E+07	-1.21E+07	1.04E+08	1.52E+07	1.52E+07	1.63E+06
12		-6.32E+05	0.00E+00	-2.54E+07	-4.6E+07	-1.21E+07	1.04E+08	1.52E+07	1.52E+07	1.30E+06
13		-6.32E+05	0.00E+00	-2.54E+07	-4.6E+07	-1.21E+07	1.04E+08	1.52E+07	1.52E+07	1.04E+06
14		-6.32E+05	0.00E+00	-2.54E+07	-4.6E+07	-1.21E+07	1.04E+08	1.52E+07	1.52E+07	8.33E+05
15		-6.32E+05	0.00E+00	-2.54E+07	-4.6E+07	-1.21E+07	1.04E+08	1.52E+07	1.52E+07	6.66E+05
16		-6.32E+05	0.00E+00	-2.54E+07	-4.6E+07	-1.21E+07	1.04E+08	1.52E+07	1.52E+07	5.33E+05
17		-6.32E+05	0.00E+00	-2.54E+07	-4.6E+07	-1.21E+07	1.04E+08	1.52E+07	1.52E+07	4.27E+05
18		-6.32E+05	0.00E+00	-2.54E+07	-4.6E+07	-1.21E+07	1.04E+08	1.52E+07	1.52E+07	3.41E+05
19		-6.32E+05	0.00E+00	-2.54E+07	-4.6E+07	-1.21E+07	1.04E+08	1.52E+07	1.52E+07	2.73E+05
20		-6.32E+05	0.00E+00	-2.54E+07	-4.6E+07	-1.21E+07	1.04E+08	1.52E+07	1.52E+07	2.18E+05
Tot.		-1.26E+07	8.43E+07	5.08E+08	9.2E+08	-2.42E+08	2.09E+09	2.40E+08	2.40E+08	0.00

Information about Industry References for base material costs.

Wood Mackenzie Chemicals data was provided by direct communication with Chris Esworthy, the director of Information Assurance Services at Aprio.

Georgia Public Service Commission data for natural gas is provided online and may be accessed at: http://www.psc.state.ga.us/content.aspx?c=/gas-marketer-pricing/.

ICIS data for glycerol and ethylene are found online through news postings on icis.com. The respective websites are: www.icis.com/explore/resources/news /2018/02/14/10193613/us-crude-glycerine-prices-could-dip-as-spring-nears/ and www.icis.com/explore/resources/news/ 2018/12/03/10290055/us-november-ethylene-settles-down-2-centslb-on-costs/

The market price for ethanol was obtained from the ethanol future market price. This may be accessed at: https://www.nasdaq.com/markets/ethanol.aspx

The market price for Methanol was obtained from a quote found online at: https://www.methanex.com/our-business/pricing

Sugar prices are from the ticker: “QYO” on the NY Mercantile Exchange. This may be accessed at https://quotes.ino.com/exchanges/exchange.html?e=NYMEX

Furfural prices were found online at: www.cnchemicals.com/Press/86385-CCM:%20Chinas%20market%20price%20of%20furfural%20bounces%20back%20in%20April.html.

APPENDIX D. SUPPLEMENTAL MATERIAL FOR CHAPTER 5

We present the supplemental material for CHAPTER 5. All formulas described are taken from (Seider, Seader et al. 2009) or (Seader, Henley et al. 1998).

D.1 Reverse Osmosis

In a reverse osmosis system, the feed is pushed through a reverse osmosis membrane and a specified pressure difference will be maintained across the membrane. The retentate will have a higher solvent concentration than the permeate. Considering this setup, the purchase cost needs to include both the pump and the membrane itself.

D.1.1 Pump

We modeled the pump as a centrifugal pump, which can handle flowrates up to 5,000 gallons per minute (gpm) and fluid head up to 3,200 ft. We chose a fluid head of 2,700 ft to provide a hydraulic pressure of 80 atm across the membrane. Because of our high feed flowrate, we split the feed into 3 pumps. The size factor for a centrifugal pump, S, is calculated in Equation 5 based on the flow rate through the pump, Q, and its head, H.

$$S = Q(H)^{0.5} \tag{5}$$

The base cost of a pump is therefore calculated in Equation 6 based on this size factor,

$$C_B = \exp\{9.7171 - 0.6019[\ln(S)] + 0.0519[\ln(S)]^2\} \tag{6}$$

To account for the different types of pump and different materials of construction, a type factor and material factor are added in to give the total purchase cost in Equation 7,

$$C_P = F_T F_M C_B \tag{7}$$

Each centrifugal pump is driven by an electric motor, whose cost is added to the pump purchase cost. The size parameter for the motor is its power consumption, P_C, which can be calculated by Equation 8,

$$P_C = \frac{QH\rho}{33{,}000\eta_P\eta_M} \tag{8}$$

The base cost of a motor is calculated based on the size factor in Equation 9,

$$\begin{aligned} C_B = \exp\{&5.8259 + 0.13141[\ln(P_C)] + 0.053255[\ln(P_C)]^2 \\ &+ 0.028628[\ln(P_C)]^3 - 0.0035549[\ln(P_C)]^4\} \end{aligned} \tag{9}$$

To account for different types of motor, a type factor is added in to give the total purchase cost in Equation 10.

$$C_P = F_T C_B \tag{10}$$

D.1.2 Membrane

To calculate the cost of the membrane needed, we investigated a few commercial membranes such as Thin-Film Composite membranes. The membrane cost depends on the area of the membrane, which can be calculated using the flux through the membrane. For a reverse osmosis membrane, the mass transport flux is described in Equation 11,

$$N_A = \frac{P_A}{l_M}(\overline{\Delta P - \Delta\pi}) = \frac{flow\ rate\ of\ permeate}{A} \tag{11}$$

where ΔP is the pressure difference across the membrane and $\Delta\pi$ is the osmotic pressure difference across the membrane. Equation 12 gives an approximation for the osmotic pressure as

$$\pi \approx RTc_B \tag{12}$$

and because the permeate is mostly water, the osmotic pressure on the permeate side is zero. The osmotic pressure from the feed increases as the solution gets concentrated, so the driving force $(\overline{\Delta P - \Delta\pi})$ is calculated by a log-mean average in Equation 13,

$$(\overline{\Delta P - \Delta\pi}) = \ln\left(\frac{P - \pi_f}{P - \pi_r}\right) \tag{13}$$

Given the permeate and retentate flow rates, the area needed for the membrane can be determined. Using this area and the commercial price of a membrane, the capital cost for a membrane is calculated.

D.2 Multiple Effect Evaporation

The capital cost calculation for the multiple effect evaporation unit is done as a series of evaporators. However, a series of flash columns and heat exchangers can be used as substitutes when modeling the unit in simulation environments that do not have a built-in evaporator unit. The most common type of evaporator is a long-tube vertical evaporator, which has a heat transfer coefficient of up to $U = 650\frac{Btu}{hr\ ft^2\ ^\circ F}$. Given the heat duty and

temperature of each evaporator, the heat transfer area A can be calculated. This is then used to compute the production cost along with the material factor F_M in Equation 14.

$$C_P = (F_M)(5700A^{0.55}) \tag{14}$$

D.3 Distillation

The distillation columns are modeled as vertical flash columns with the addition of a tray cost C_T added to the purchasing cost. The cost of an empty vertical column, which includes any nozzles and support, is calculated in Equation 15 as

$$C_V = \exp\{7.2756 + 0.18255[\ln(W)] + 0.02297[\ln(W)]^2\} \tag{15}$$

Added to this is the added cost for platforms and ladders as shown in Equation 16,

$$C_{PL} = 300.9(D)^{0.73960}(L)^{0.70684} \tag{16}$$

To calculate the cost for the trays, a base cost is calculated first in Equation 17,

$$C_{BT} = 468\exp(0.1739D) \tag{17}$$

Then, factors are multiplied in to take into account the tray type (F_{TT}), the material of construction (F_{TM}), and the number of trays (F_{NT}). The number of trays can be obtained from the theoretical number specified in ASPEN+ using the tray efficiency in Equation 18,

$$\#\ trays\ actual = E_T * (\#\ trays\ theoretical) \tag{18}$$

The total cost of the trays and the total purchasing costs are therefore,

$$C_T = N_T F_{TT} F_{MT} F_{NT} C_{BT} \quad (19)$$

and

$$C_P = F_M C_V + C_{PL} + C_T \quad (20)$$

respectively.

Reboiler and condenser costs are calculated in ASPEN+ for each scenario. These costs include the condenser, the condenser accumulator, the reboiler, and the reflux heat pump. While a significant fraction of the overall capital cost for the distillation units, changes to the capital costs have little impact on the required lignin selling price due to the high energy requirements to boil off all the water.

D.4 Operating Costs

The values used for operating costs are given in Table D.1,

Table D.1. Cost factors used for utilities (Seider, Seader et al. 2009).

Cost Factor	Typical Factor
HP Steam, 450 psig	\$14.50/1000 kg
MP Steam, 150 psig	\$10.50/1000 kg
LP Steam, 50 psig	\$6.60/1000 kg
Electricity	\$0.06/kW-h
Cooling water	\$0.02/m^3

D.5 Cash Flow Calculations

The assumptions made in these calculations are as follows:

- The sum of the installed costs makes up the total depreciable capital
- Service life is 20 years
- The capital cost is paid yearly to an annuity at a 5% nominal interest rate, where interest compounds yearly
- Salvage value of the equipment is $0
- No revenue is considered

The annuity payment is calculated using a discrete uniform-series capital-recovery factor which is given in Equation 21 as,

$$A = P * \frac{i(1+i)^n}{(1+i)^n - 1} \tag{21}$$

where n is the number of interest periods over the course of the payments. Based on yearly payments and annual compound interest, n = 20. This value is added to the total operating cost to obtain a total annual cost. To represent the annual total cost in terms of $/kg lignin, this sum is divided by the annual lignin production rate.

D.6 ASPEN+ Simulations

The high-boiling simulations are run using two components: DMSO and water. The base method chosen is NRTL. The low-boiling simulations are run using ethanol and water, and the base method chosen is UNIFAC. The membrane pump was modeled using a PUMP unit with a specified pressure increase of 80 atm and efficiencies (pump and motor) of 0.9. The evaporator was simulated as a series of flash columns and heaters, where the energy output of one heater is fed into the next flash column (Vazquez-Rojas, Garfias-Vásquez et al. 2018). A steam input (at 130°C, 2 atm) provides the energy for the first flash column,

and the temperature and pressure differences between each subsequent heater/flash units determine the final solvent concentration. The total steam inputs and temperature specifications for the evaporators are shown in Table D.2 and Table D.3 respectively.

Table D.2. Steam inputs and for each evaporator scenario.

Starting solvent %	Final solvent %	Steam input [kg/hr]
10%	30%	340,000
10%	40%	375,000
10%	70%	430,000
10%	90%	448,000
24%	70%	140,000
24%	90%	159,000

Table D.3. Temperature and pressure for each evaporator effect.

Effect	Temperature [°C]	Pressure [atm]
1	100	1
2	96.71	0.9
3	93.51	0.8
4	89.96	0.7
5	85.95	0.6

The distillation columns had two different setups: one for high-boiling solvents and one for low-boiling. In both cases, the variables specified were mass recovery and mass purity of the solvent. A multiplier unit was added to reduce the feed flow rate to an industrially feasible amount, and the multiplier factor differs depending on the total feed flow rate and desired mass purity in the product.

Table D.4. Distillation column specifications used in ASPEN+.

	# theoretical stages	Mass recovery %
High-boiling	6	99.5
Low-boiling	15	99.5

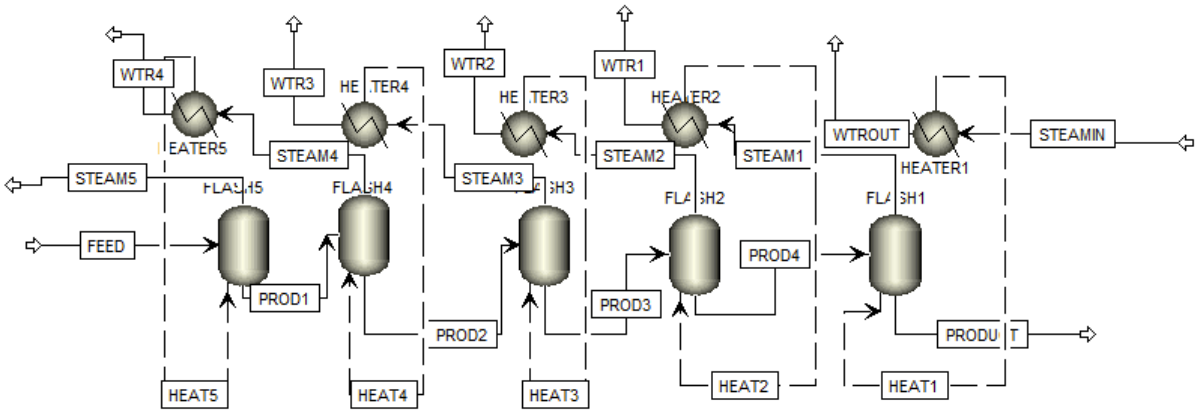


Figure D.1. ASPEN+ process flow diagram of a five-effect evaporator. The final product comes out in the PRODUCT stream.

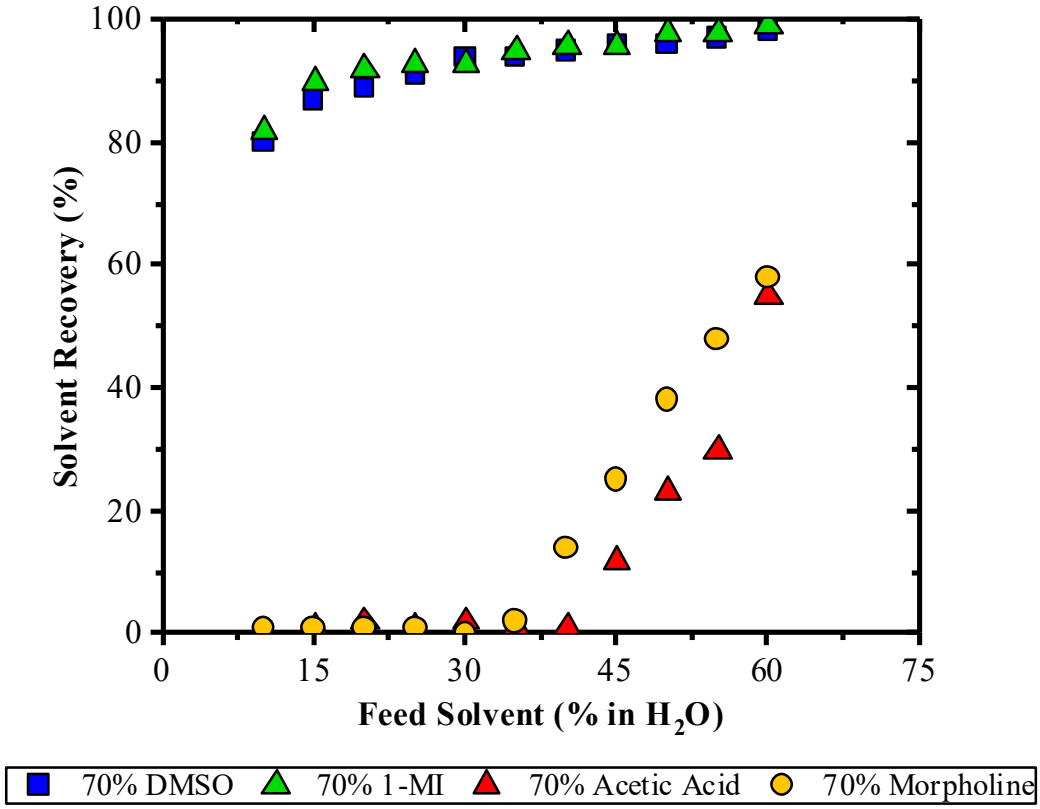


Figure D.2. Achievable solvent recovery for evaporator unit to reach 70% solvent purity at various feed concentrations. Two high-boiling solvents of high relative volatility (1-MI and DMSO) are compared to two with low relative volatilities (Acetic Acid and Morpholine).

APPENDIX E. SUPPLEMENTAL MATERIAL FOR CHAPTER 6

This work presents supplemental material for the different solvent selection screens presented in CHAPTER 6.

E.1 Hazard & Exposure

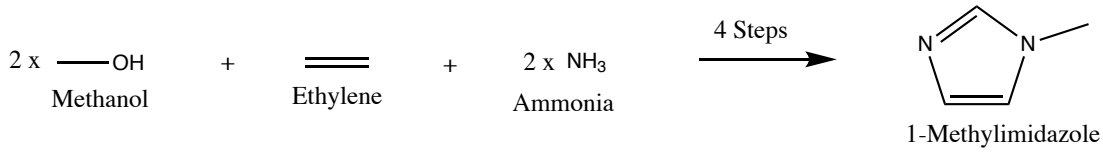
For the hazard & exposure criteria that builds on a CHEM21 hazard & environmental scoring system, we utilized an open access excel spreadsheet in the supplementary data file of (Prat, Wells et al. 2015). This excel file may be accessed directly online at: http://www.rsc.org/suppdata/c5/gc/c5gc01008j/c5gc01008j1.xlsx

For each solvent, we used a published methodology to calculate safety, health, and environmental scores (e.g. 1, 7, 5) and entered that data into the "solvent data sheet" sheet in columns CZ – DB. By using the embedded tools, the CHEM21 recommendations are presented in columns DP and DQ.

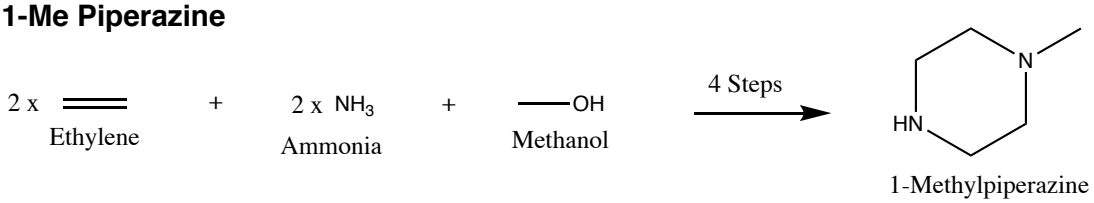
E.2 Cost & Availability

The industrial synthesis routes were explored for each solvent. As discussed in SECTION 6.3.3, the base materials and number of steps were calculated for each solvent. These values are presented in **Error! Reference source not found.**. Industrial synthesis routes were found for all chemicals except 2-methylpiperidine. This reaction was predicted based on similar chemical production routes.

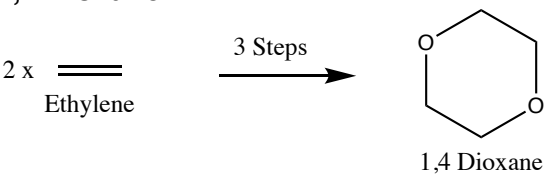
1 - Methylimidazole



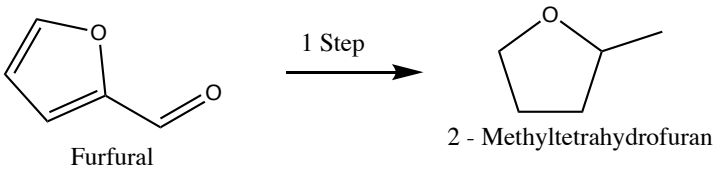
1-Me Piperazine



1,4 Dioxane



2 - Me THF



2-Hexanone

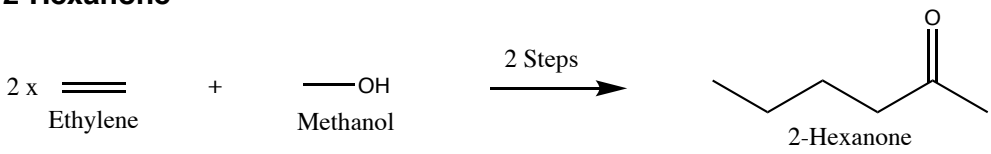
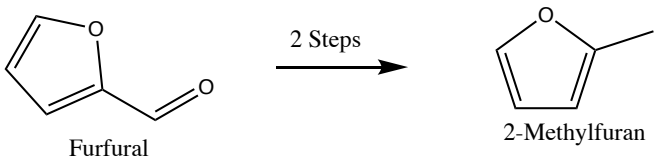
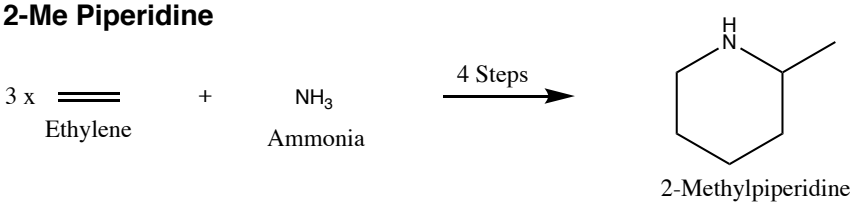


Figure E.1. Base materials and synthesis steps for each organic solvent.

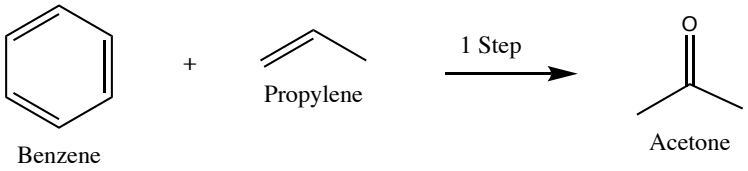
2-Me Furan



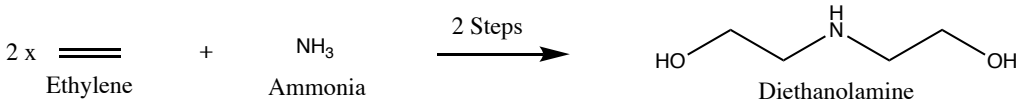
2-Me Piperidine



Acetone



Diethanolamine



DMSO

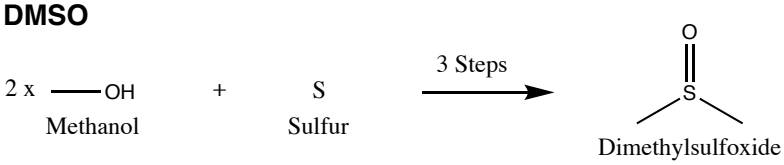
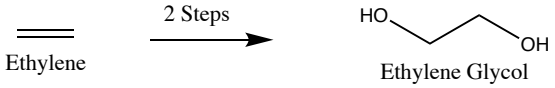
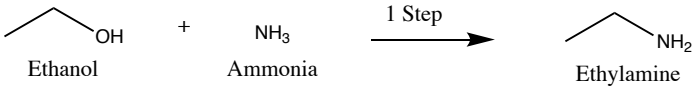


Figure E.1 Continued. Base materials and synthesis steps for each organic solvent.

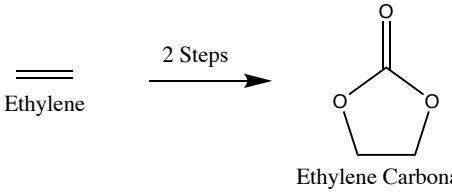
Ethylene Glycol



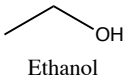
Ethylamine



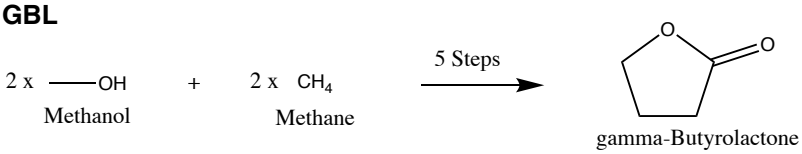
Ethylene Carbonate



Ethanol



GBL



GVL

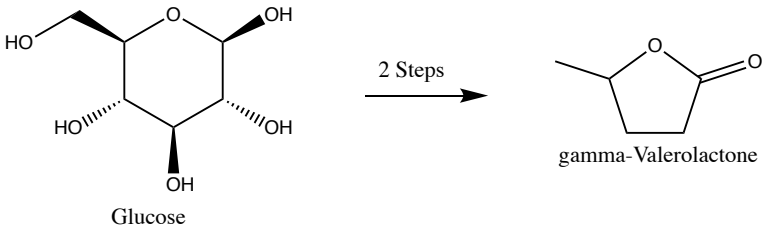
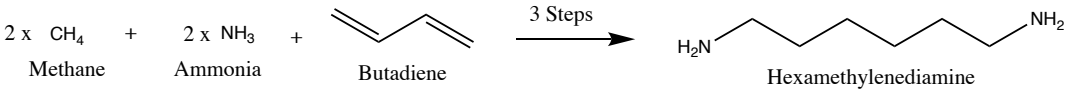


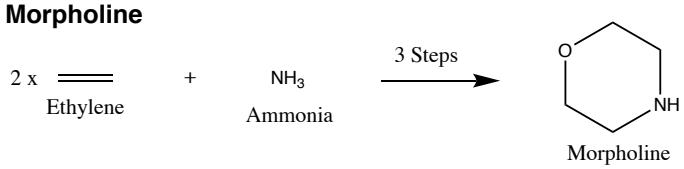
Figure E.1 Continued. Base materials and synthesis steps for each organic solvent.

Hexamethylenediamine

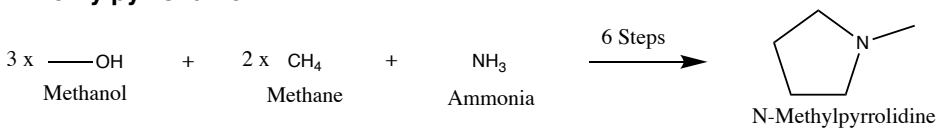


Methanol

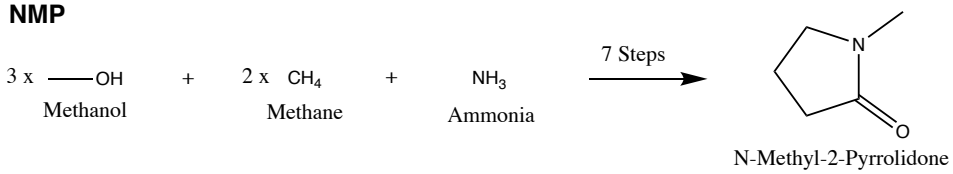
Morpholine



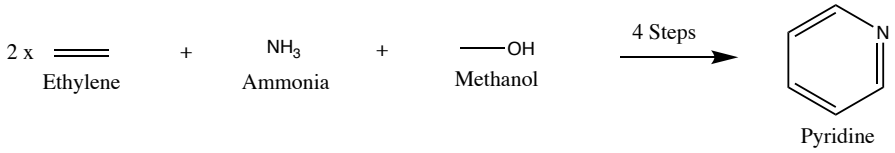
N-Methylpyrrolidine



NMP



Pyridine



Piperidine

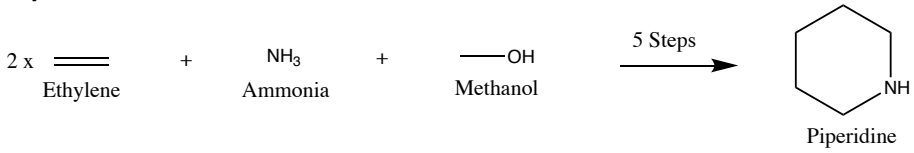
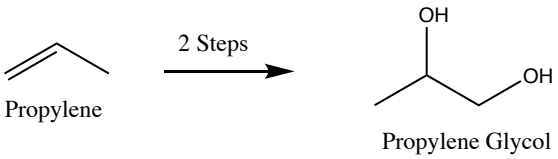
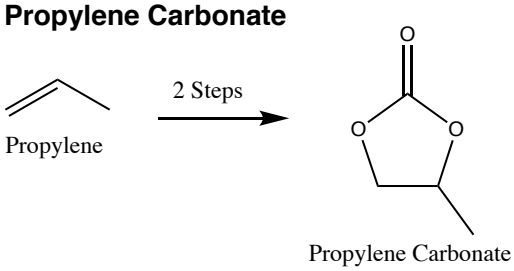


Figure E.1 Continued. Base materials and synthesis steps for each organic solvent.

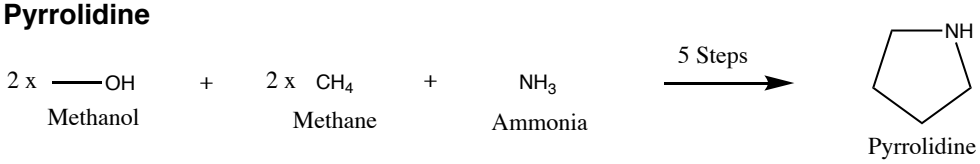
Propylene Glycol



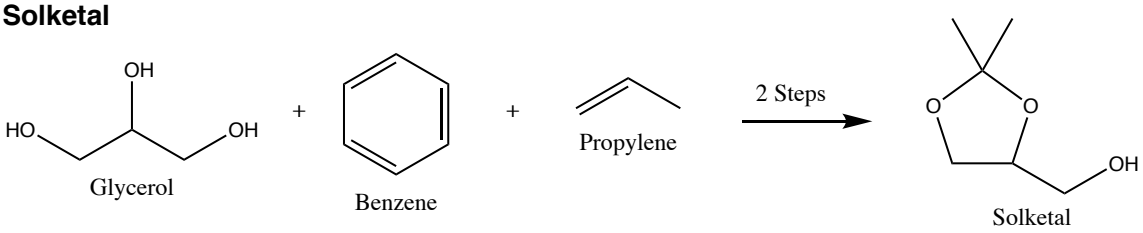
Propylene Carbonate



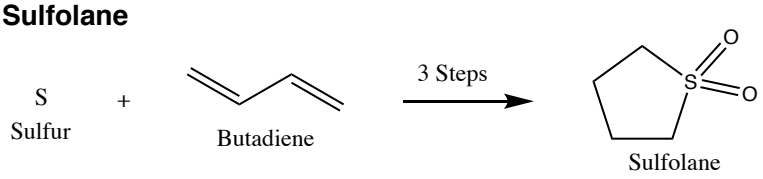
Pyrrolidine



Solketal



Sulfolane



THF

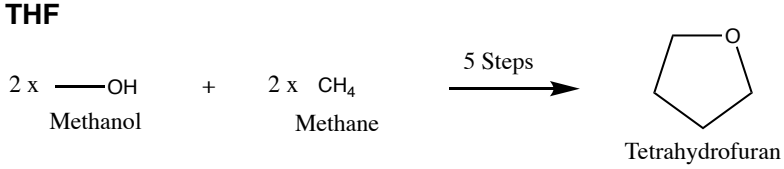
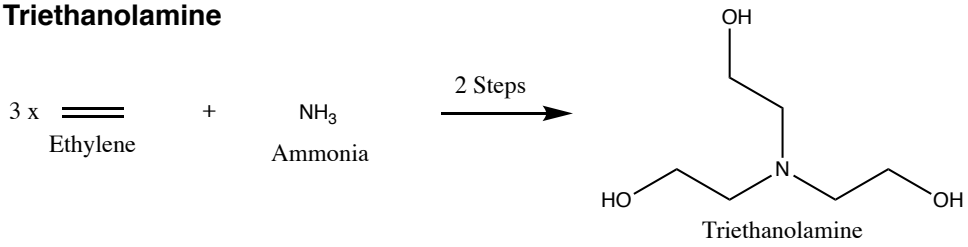
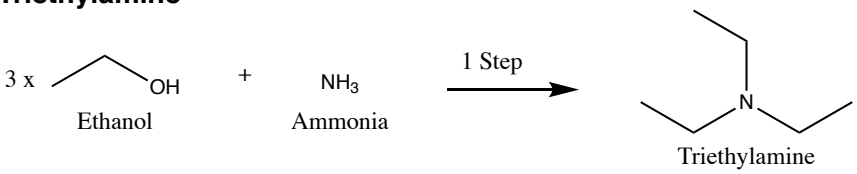


Figure E.1 Continued. Base materials and synthesis steps for each organic solvent.

Triethanolamine



Triethylamine



Water

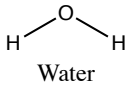


Figure E.1 Continued. Base materials and synthesis steps for each organic solvent.

REFERENCES

Abuja, P., M. Schmuck, I. Pilz, P. Tomme, M. Claeyssens and H. Esterbauer (1988). "Structural and functional domains of cellobiohydrolase I from Trichoderma reesei." European Biophysics Journal **15**(6): 339-342.

ACS (2011). "Solvent Selection Guide: Version 2.0." ACS Green Chemistry Institute® Pharmaceutical Roundtable.

Al-Dajani, W. W., U. W. Tschirner and T. Jensen (2009). "Pre-extraction of hemicelluloses and subsequent kraft pulping Part II: Acid-and autohydrolysis." TAPPI Journal **8**(9): 30-37.

Alfonsi, K., J. Colberg, P. J. Dunn, T. Fevig, S. Jennings, T. A. Johnson, H. P. Kleine, C. Knight, M. A. Nagy and D. A. Perry (2008). "Green chemistry tools to influence a medicinal chemistry and research chemistry based organisation." Green Chemistry **10**(1): 31-36.

Alizadeh, H., F. Teymouri, T. I. Gilbert and B. E. Dale (2005). "Pretreatment of switchgrass by ammonia fiber explosion (AFEX)." Applied biochemistry biotechnology bioengineering **124**(1-3): 1133-1141.

Almeida, D., R. Santos, P. Hart and H. Jameel (2015). "Hardwood pulping kinetics of bulk and residual phases." TAPPI Journal **14**(10): 652-662.

Alriols, M. G., A. Tejado, M. a. Blanco, I. Mondragon and J. Labidi (2009). "Agricultural palm oil tree residues as raw material for cellulose, lignin and hemicelluloses production by ethylene glycol pulping process." Chemical Engineering Journal **148**(1): 106-114.

Andanson, J.-M., E. Bordes, J. Devémy, F. Leroux, A. A. Pádua and M. F. C. Gomes (2014). "Understanding the role of co-solvents in the dissolution of cellulose in ionic liquids." Green Chemistry **16**(5): 2528-2538.

Atkins, M., M. Walmsley, A. Morrison and J. Neale (2012). "Process integration in pulp and paper mills for energy and water reduction-A review." Appita Journal: Journal of the Technical Association of the Australian New Zealand Pulp Paper Industry **65**(2): 170.

Axegård, P., N. Berglin, K. Lindgren, P. Tomani and F. Öhman (2011). The kraft pulp mill biorefinery platform. 5th International Colloquium on Eucalyptus Pulp, Porto Seguro, Bahia, Brazil.

Axelsson, E., M. R. Olsson and T. Berntsson (2006). "Increased capacity in kraft pulp mills: Lignin separation and reduced steam demand compared with recovery boiler upgrade." Nordic Pulp Paper Research Journal **21**(4): 485-492.

Baker, D. A. and T. G. Rials (2013). "Recent advances in low-cost carbon fiber manufacture from lignin." Journal of Applied Polymer Science **130**(2): 713-728.

Balogh, D. T., A. A. d. S. Curvelo and R. A. M. C. De Groote (1992). "Solvent effects on organosolv lignin from Pinus caribaea hondurensis." Holzforschung-International Journal of the Biology, Chemistry, Physics Technology of Wood **46**(4): 343-348.

Bansal, P., M. Hall, M. J. Realff, J. H. Lee and A. S. Bommarius (2009). "Modeling cellulase kinetics on lignocellulosic substrates." Biotechnology advances **27**(6): 833-848.

Bansal, P., B. J. Vowell, M. Hall, M. J. Realff, J. H. Lee and A. S. Bommarius (2012). "Elucidation of cellulose accessibility, hydrolysability and reactivity as the major limitations in the enzymatic hydrolysis of cellulose." Bioresource technology **107**: 243-250.

Baral, N. R. and A. Shah (2016). "Techno-economic analysis of cellulose dissolving ionic liquid pretreatment of lignocellulosic biomass for fermentable sugars production." Biofuels, Bioproducts, Biorefining **10**(1): 70-88.

Bastidas, P., J. Parra, I. Gil and G. Rodríguez (2012). "Alcohol distillation plant simulation: thermal and hydraulic studies." Procedia Engineering **42**: 80-89.

Blain, T. J. (1993). "Anthraquinone pulping: fifteen years later." TAPPI Journal **76**: 137-142.

Brebu, M. and C. Vasile (2010). "Thermal degradation of lignin—a review." Cellulose Chemistry Technology **44**(9): 353.

Brethauer, S. and C. E. Wyman (2010). "Continuous hydrolysis and fermentation for cellulosic ethanol production." Bioresource technology **101**(13): 4862-4874.

Brewster, J. (2007). Economic impact of modern kraft recovery boilers. International chemical recovery conference, Quebec City, Canada.

Brownell, H., E. Yu and J. Saddler (1986). "Steam-explosion pretreatment of wood: Effect of chip size, acid, moisture content and pressure drop." Biotechnology bioengineering **28**(6): 792-801.

Brundtland, G. (1987). Our Common Future: Report of the World Commission on Environment and Development, Geneva, UN Document A/42/427.

Cai, C. M., T. Zhang, R. Kumar and C. E. Wyman (2013). "THF co-solvent enhances hydrocarbon fuel precursor yields from lignocellulosic biomass." Bioresource technology **15**(11): 3140-3145.

Cantarella, M., L. Cantarella, A. Gallifuoco, A. Spera and F. Alfani (2004). "Effect of inhibitors released during steam-explosion treatment of poplar wood on subsequent enzymatic hydrolysis and SSF." Biotechnology progress **20**(1): 200-206.

Chakar, F. S. and A. J. Ragauskas (2004). "Review of current and future softwood kraft lignin process chemistry." Industrial Crops and Products **20**(2): 131-141.

Chandra, R., S. Ewanick, C. Hsieh and J. N. Saddler (2008). "The characterization of pretreated lignocellulosic substrates prior to enzymatic hydrolysis, part 1: a modified Simons' staining technique." Biotechnology progress **24**(5): 1178-1185.

Chandra, R. P., V. Arantes and J. Saddler (2015). "Steam pretreatment of agricultural residues facilitates hemicellulose recovery while enhancing enzyme accessibility to cellulose." Bioresource technology **185**: 302-307.

Chandra, R. P. and J. N. Saddler (2012). "Use of the Simons' staining technique to assess cellulose accessibility in pretreated substrates." Industrial Biotechnology **8**(4): 230-237.

Chen, L., J. Dou, Q. Ma, N. Li, R. Wu, H. Bian, D. J. Yelle, T. Vuorinen, S. Fu and X. Pan (2017). "Rapid and near-complete dissolution of wood lignin at≤ 80° C by a recyclable acid hydrotrope." Science advances **3**(9): e1701735.

Chen, Y., Y. Wang, J. Wan and Y. Ma (2010). "Crystal and pore structure of wheat straw cellulose fiber during recycling." Cellulose **17**(2): 329-338.

Chrisandina, N. J., T. T. Kwok, A. S. Bommarius and M. J. Realff (2019). "Techno-economic analysis of water precipitation for lignin value prior to pulping." Chemical Engineering Research & Design **143**: 4-10.

Chum, H. L., L. Douglas, D. Feinberg and H. Schroeder (1985). Evaluation of pretreatments of biomass for enzymatic hydrolysis of cellulose.[Organosolv process, wet oxidation, and steam explosion of wood chips]. United States.

Chundawat, S. P., R. Vismeh, L. N. Sharma, J. F. Humpula, L. da Costa Sousa, C. K. Chambliss, A. D. Jones, V. Balan and B. E. Dale (2010). "Multifaceted characterization of cell wall decomposition products formed during ammonia fiber expansion (AFEX) and dilute acid based pretreatments." Bioresource Technology **101**(21): 8429-8438.

Claus, I., O. Kordsachia, N. Schröder and T. Karstens (2004). "Monoethanolamine (MEA) pulping of beech and spruce wood for production of dissolving pulp." Holzforschung **58**(6): 573-580.

Cohen, J. and T. Lewandowski (2016). "Alternatives assessment: On the hunt for safer chemicals." Gradient Trends - Risk Science & Applications **66**: 3-4.

Constant, S., H. L. Wienk, A. E. Frissen, P. de Peinder, R. Boelens, D. S. Van Es, R. J. Grisel, B. M. Weckhuysen, W. J. Huijgen and R. J. Gosselink (2016). "New insights into the structure and composition of technical lignins: a comparative characterisation study." Green Chemistry **18**(9): 2651-2665.

Courchene, C. E. (1998). The tried, the true, and the new-getting more pulp from chips modifications to the kraft process for increased yield. Breaking Pulp Yield Barrier Symposium. Atlanta, TAPPI**:** 11-20.

Czernik, S., R. French, C. Feik and E. Chornet (2002). "Hydrogen by catalytic steam reforming of liquid byproducts from biomass thermoconversion processes." Industrial & Engineering Chemistry Research **41**(17): 4209-4215.

da Costa Sousa, L., S. P. Chundawat, V. Balan and B. E. Dale (2009). "'Cradle-to-grave'assessment of existing lignocellulose pretreatment technologies." Current opinion in biotechnology **20**(3): 339-347.

Dahl, G. (1884). Process of manufacturing cellulose from wood. US Patent 296,935. United States.

Davis, R., L. Tao, E. Tan, M. Biddy, G. Beckham, C. Scarlata, J. Jacobson, K. Cafferty, J. Ross and J. Lukas (2013). Process design and economics for the conversion of lignocellulosic biomass to hydrocarbons: dilute-acid and enzymatic deconstruction of biomass to sugars and biological conversion of sugars to hydrocarbons, National Renewable Energy Lab.(NREL), Golden, CO (United States).

de Assis, C. A., L. G. Greca, M. Ago, M. Y. Balakshin, H. Jameel, R. Gonzalez and O. J. Rojas (2018). "Techno-Economic Assessment, Scalability, and Applications of Aerosol Lignin Micro-and Nanoparticles." ACS sustainable chemistry & engineering **6**(9): 11853.

DEA (2000). "Placement of gamma-butyrolactone in List I of the Controlled Substances Act (21 U. S.C. 802(34)). ." Drug Enforcement Administration **65**(79): 21645–21647.

Dinwiddie, J. G. (1938). Method and apparatus for drying. US Patent 2,139,445. United States.

Donohoe, B. S., S. R. Decker, M. P. Tucker, M. E. Himmel and T. B. Vinzant (2008). "Visualizing lignin coalescence and migration through maize cell walls following thermochemical pretreatment." Biotechnology and bioengineering **101**(5): 913-925.

Dorez, G., L. Ferry, R. Sonnier, A. Taguet and J.-M. Lopez-Cuesta (2014). "Effect of cellulose, hemicellulose and lignin contents on pyrolysis and combustion of natural fibers." Journal of Analytical and Applied Pyrolysis **107**: 323-331.

Duarte, G. V., B. V. Ramarao, T. E. Amidon and P. T. Ferreira (2011). "Effect of hot water extraction on hardwood kraft pulp fibers (Acer saccharum, sugar maple)." Industrial Engineering Chemistry Research **50**(17): 9949-9959.

El-Halwagi, M. M. and V. Manousiouthakis (1989). "Synthesis of mass exchange networks." AIChE Journal **35**(8): 1233-1244.

Fair, J. R. (1997). Perry's Chemical Engineers' Handbook. New York, McGraw-Hill.

FAOSTAT (2018). Forest Products Statistics, Food and Agricultural Organization of the United Nations.

Fardim, P. and N. Durán (2004). "Retention of cellulose, xylan and lignin in kraft pulping of eucalyptus studied by multivariate data analysis: influences on physicochemical and mechanical properties of pulp." Journal of the Brazilian Chemical Society **15**(4): 514-522.

Fatehi, P. and J. Chen (2016). Extraction of technical lignins from pulping spent liquors, challenges and opportunities. Production of Biofuels and Chemicals from Lignin, Springer**:** 35-54.

FDA (2018). "Guidance for Industry: Q3C—Tables and List " USHaH Services: Silver Spring, MD, USA.

Ferrini, P. and R. Rinaldi (2014). "Catalytic biorefining of plant biomass to non-pyrolytic lignin bio-oil and carbohydrates through hydrogen transfer reactions." Angewandte Chemie International Edition **53**(33): 8634-8639.

ForeverPure (2018). Filmtec SW30HRLE-400 Sea Water Desalination Membrane. https://www.foreverpureplace.com/Filmtec-SW30HRLE-400-Sea-Water-Desalination-Membra-p/sw30hrle-400.htm.

Frolkova, A. and V. Raeva (2010). "Bioethanol dehydration: state of the art." Theoretical Foundations of Chemical Engineering **44**(4): 545-556.

Gellerstedt, G. and E.-L. Lindfors (1984). "Structural changes in lignin during kraft pulping." Holzforschung-International Journal of the Biology, Chemistry, Physics Technology of Wood **38**(3): 151-158.

George, A., A. Brandt, K. Tran, S. M. N. S. Zahari, D. Klein-Marcuschamer, N. Sun, N. Sathitsuksanoh, J. Shi, V. Stavila and R. Parthasarathi (2015). "Design of low-cost ionic liquids for lignocellulosic biomass pretreatment." Green Chemistry **17**(3): 1728-1734.

Gericke, M., P. Fardim and T. Heinze (2012). "Ionic liquids—promising but challenging solvents for homogeneous derivatization of cellulose." Molecules **17**(6): 7458-7502.

Gharehkhani, S., E. Sadeghinezhad, S. N. Kazi, H. Yarmand, A. Badarudin, M. R. Safaei and M. N. M. Zubir (2015). "Basic effects of pulp refining on fiber properties—a review." Carbohydrate polymers **115**: 785-803.

Goodell, B., D. Nicholas and T. Schultz (2001). Current knowledge of wood deterioration mechanisms and its impact on biotechnology and wood preservation. Symposium at the 221st National Meeting of the American Chemical Society, San Diego, California, USA, American Chemical Society.

Gould, J. M. (1984). "Alkaline peroxide delignification of agricultural residues to enhance enzymatic saccharification." Biotechnology bioengineering **26**(1): 46-52.

Gourlay, K., V. Arantes and J. N. Saddler (2012). "Use of substructure-specific carbohydrate binding modules to track changes in cellulose accessibility and surface morphology during the amorphogenesis step of enzymatic hydrolysis." Biotechnology for biofuels **5**(1): 51.

Grohmann, K., R. Torget, M. Himmel and C. Scott (1986). Dilute acid pretreatment of biomass at high acid concentrations. Biotechnology Bioengineering Symposium, Golden, CO, Solar Energy Research Institute.

Gullichsen, J. and C.-J. Fogelholm (1999). Papermaking Science and Technology, Book 6A, Chemical Pulping. Helsinki, Finland, Fapet Oy.

Hall, M., P. Bansal, J. H. Lee, M. J. Realff and A. S. Bommarius (2010). "Cellulose crystallinity–a key predictor of the enzymatic hydrolysis rate." The FEBS journal **277**(6): 1571-1582.

Hansen, C. M. (2002). Hansen solubility parameters: a user's handbook, CRC press.

Hart, P. W. and A. W. Rudie (2014). "Anthraquinone-A review of the rise and fall of a pulping catalyst." TAPPI Journal **13**(10): 23-31.

Hartler, N. (1959). "Sulphate cooking with the addition of reducing agents. Part 1. Preliminary report on the addition of sodium borohydride." Svensk Papperstidning **62**(13): 467-470.

Helmerius, J., J. V. von Walter, U. Rova, K. A. Berglund and D. B. Hodge (2010). "Impact of hemicellulose pre-extraction for bioconversion on birch Kraft pulp properties." Bioresource technology **101**(15): 5996-6005.

Henderson, M. and A. Hjort (2016). Addition of new washers to an existing brown stock wash line. Paper Week Canada. Montreal, Canada.

Henderson, R. K., C. Jiménez-González, D. J. Constable, S. R. Alston, G. G. Inglis, G. Fisher, J. Sherwood, S. P. Binks and A. D. Curzons (2011). "Expanding GSK's solvent selection guide–embedding sustainability into solvent selection starting at medicinal chemistry." Green Chemistry **13**(4): 854-862.

Henrissat, B. (1994). "Cellulases and their interaction with cellulose." Cellulose **1**(3): 169-196.

Herrick, F. W., R. L. Casebier, J. K. Hamilton and K. R. Sandberg (1983). Microfibrillated cellulose: morphology and accessibility. Applied Polymer Symposium, Shelton, WA, ITT Rayonier Inc.

Himmel, M. E., S.-Y. Ding, D. K. Johnson, W. S. Adney, M. R. Nimlos, J. W. Brady and T. D. Foust (2007). "Biomass recalcitrance: engineering plants and enzymes for biofuels production." Science **315**(5813): 804-807.

Holladay, J. E., J. F. White, J. J. Bozell and D. Johnson (2007). Top value-added chemicals from biomass-Volume II—Results of screening for potential candidates from biorefinery lignin, Pacific Northwest National Lab.(PNNL), Richland, WA, USA.

Holton, H. H. (1977). Delignification of lignocellulosic material with an alkaline liquor in the presence of a cyclic keto compound. US Patent 4,012,280. United States.

Hu, Z., X. Du, J. Liu, H.-m. Chang and H. Jameel (2016). "Structural characterization of pine kraft lignin: BioChoice lignin vs Indulin AT." Journal of Wood Chemistry and Technology **36**(6): 432-446.

Humbird, D., R. Davis, L. Tao, C. Kinchin, D. Hsu, A. Aden, P. Schoen, J. Lukas, B. Olthof and M. Worley (2011). Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol: dilute-acid pretreatment and enzymatic hydrolysis of corn stover, National Renewable Energy Lab.(NREL), Golden, CO, USA.

Inalbon, M. C., M. C. Mussati, P. Mocchiutti and M. A. Zanuttini (2011). "Modeling of alkali impregnation of eucalyptus wood." Industrial & Engineering Chemistry Research **50**(5): 2898-2904.

Inglesby, M. and S. Zeronian (1996). "The accessibility of cellulose as determined by dye adsorption." Cellulose **3**(1): 165-181.

Jackson, B. D. (2016). Georgia Timber Price Report. Georgia Forestry Statistics, University of Georgia**:** http://gaforestrystats.info/prices/georgia-timber-price-report-2016-2011st-quarter.

Jenkins, S. (2018). "CEPCI Updates: January 2018 (prelim.) and December 2017 (final)." Chemical Engineering-Page **1**: 30.

Jiménez, L., A. Perez, M. De la Torre, A. Rodríguez and V. Angulo (2008). "Ethyleneglycol pulp from tagasaste." Bioresource technology **99**(7): 2170-2176.

Johansson, A., O. Aaltonen and P. Ylinen (1987). "Organosolv pulping—methods and pulp properties." Biomass **13**(1): 45-65.

Joly, C. A. and L. Verdade (2015). "Bioenergy & sustainability: bridging the gaps." SCOPE, Paris, France.

Julien, L. M. and E. W. Malcolm (1978). "Amine solvent pulping. Project 3354-1, report one: a progress report to members of the Institute of Paper Chemistry." Appleton, Wisconsin, USA.

Kaar, W., C. Gutierrez and C. Kinoshita (1998). "Steam explosion of sugarcane bagasse as a pretreatment for conversion to ethanol." Biomass Bioenergy **14**(3): 277-287.

Kajzer, W. and J. Bowie (2007). Recovery of pin chips from a chip washing reject stream. US Patent 20,070,045,157. United States.

Kanchanalai, P., R. P. Lively, M. J. Realff and Y. Kawajiri (2013). "Cost and energy savings using an optimal design of reverse osmosis membrane pretreatment for dilute bioethanol purification." Industrial Engineering Chemistry Research **52**(32): 11132-11141.

Kang, Y., M. J. Realff, M. Sohn, J. H. Lee and A. S. Bommarius (2015). "An effective chemical pretreatment method for lignocellulosic biomass with substituted imidazoles." Biotechnology progress **31**(1): 25-34.

Kautto, J., M. J. Realff and A. J. Ragauskas (2013). "Design and simulation of an organosolv process for bioethanol production." Biomass Conversion and Biorefinery **3**(3): 199-212.

Kautto, J., M. J. Realff, A. J. Ragauskas and T. Kässi (2014). "Economic analysis of an organosolv process for bioethanol production." BioResources **9**(4): 6041-6072.

Kautto, J., E. Saukkonen and K. Henricson (2010). "Digestibility and paper-making properties of prehydrolyzed softwood chips." BioResources **5**(4): 2502-2519.

Kazi, F. K., J. A. Fortman, R. P. Anex, D. D. Hsu, A. Aden, A. Dutta and G. Kothandaraman (2010). "Techno-economic comparison of process technologies for biochemical ethanol production from corn stover." Fuel **89**: S20-S28.

Kevlich, N. S., M. L. Shofner and S. Nair (2017). "Membranes for kraft black liquor concentration and chemical recovery: Current progress, challenges, and opportunities." Separation Science and Technology **52**(6): 1070-1094.

Kim, Y. S. and R. H. Newman (1995). Solid state 13C NMR study of wood degraded by the brown rot fungus Gloeophyllum trabeum, Walter de Gruyter, Berlin/New York.

Kirk-Othmer (2004). Kirk-Othmer encyclopedia of chemical technology, Wiley Interscience Imprint.

Klein-Marcuschamer, D., B. A. Simmons and H. W. Blanch (2011). "Techno-economic analysis of a lignocellulosic ethanol biorefinery with ionic liquid pre-treatment." Biofuels, Bioproducts and Biorefining **5**(5): 562-569.

Kondo, R. and J. L. McCarthy (1985). "Condensation of lignins with coniferyl alcohol in alkaline aqueous solutions." Journal of wood chemistry technology **5**(1): 37-52.

Kouisni, L., P. Holt-Hindle, K. Maki and M. Paleologou (2012). "The lignoforce system: a new process for the production of high-quality lignin from black liquor." Journal of Science and Technology for Forest Products and Processes **2**(4): 6-10.

Koyama, K., T. Nishi, I. Hashida and M. Nishimura (1982). "The rejection of polar organic solutes in aqueous solution by an interpolymer anionic composite reverse osmosis membrane." Journal of Applied Polymer Science **27**(8): 2845-2855.

Kubo, S. and J. F. Kadla (2004). "Poly (ethylene oxide)/organosolv lignin blends: Relationship between thermal properties, chemical structure, and blend behavior." Macromolecules **37**(18): 6904-6911.

Kumar, P., D. M. Barrett, M. J. Delwiche and P. Stroeve (2009). "Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production." Industrial engineering chemistry research **48**(8): 3713-3729.

Kwok, T. T., C. O. Luettgen, M. J. Realff and A. S. Bommarius (2017). "Lignin value prior to pulping (LVPP): An advanced pulping concept." TAPPI Journal **16**(10): 553-555.

Laakso, O. A. (1969). Cellulose digester with washing apparatus. US Patent 3,475,271. United States.

Laure, S., M. Leschinsky, M. Fröhling, F. Schultmann and G. Unkelbach (2014). "Assessment of an organosolv lignocellulose biorefinery concept based on a material flow analysis of a pilot plant." Cellulose Chemistry and Technology **48**(9-10): 793-798.

Lee, J.-W., K.-S. Gwak, J.-Y. Park, M.-J. Park, D.-H. Choi, M. Kwon and I.-G. Choi (2007). "Biological pretreatment of softwood Pinus densiflora by three white rot fungi." The Journal of Microbiology **45**(6): 485-491.

Lesar, B., M. Humar, G. Hora, P. Hachmeister, D. Schmiedl, E. Pindel, M. Siika-Aho and T. Liitiä (2016). "Utilization of recycled wood in biorefineries: preliminary results of steam explosion and ethanol/water organosolv pulping without a catalyst." European Journal of Wood Wood Products **74**(5): 711-723.

Ligero, P., J. J. Villaverde, A. de Vega and M. Bao (2008). "Delignification of Eucalyptus globulus saplings in two organosolv systems (formic and acetic acid): Preliminary analysis of dissolved lignins." Industrial Crops and Products **27**(1): 110-117.

Luo, X. and J. Zhu (2011). "Effects of drying-induced fiber hornification on enzymatic saccharification of lignocelluloses." Enzyme microbial technology **48**(1): 92-99.

Luterbacher, J. S., J. M. Rand, D. M. Alonso, J. Han, J. T. Youngquist, C. T. Maravelias, B. F. Pfleger and J. A. Dumesic (2014). "Nonenzymatic sugar production from biomass using biomass-derived γ-valerolactone." Science **343**(6168): 277-280.

Lynd, L. R., X. Liang, M. J. Biddy, A. Allee, H. Cai, T. Foust, M. E. Himmel, M. S. Laser, M. Wang and C. E. Wyman (2017). "Cellulosic ethanol: status and innovation." Current opinion in biotechnology **45**: 202-211.

Malkov, S., P. Tikka and J. Gullichsen (2001). "Towards complete impregnation of wood chips with aqueous solutions." Paper and Timber **83**(8).

Mansfield, S. D., C. Mooney and J. N. Saddler (1999). "Substrate and enzyme characteristics that limit cellulose hydrolysis." Biotechnology progress **15**(5): 804-816.

Marcoccia, B., J. Prough, J. Engström and J. Gullichsen (1999). "Continuous cooking applications." Papermaking Science and Technology, Book A **6**: A513-A570.

McBride, H. (2015). New IRENA Platform Supports Renewable Energy Innovation, Quality and Collaboration, IRENA.

McDonough, T. J. (1992). "The chemistry of organosolv delignification." TAPPI Journal **76**: 186-193.

Mellmer, M. A., C. Sanpitakseree, B. Demir, P. Bai, K. Ma, M. Neurock and J. A. Dumesic (2018). "Solvent-enabled control of reactivity for liquid-phase reactions of biomass-derived compounds." Nature Catalysis **1**(3): 199.

Meng, X. and A. J. Ragauskas (2014). "Recent advances in understanding the role of cellulose accessibility in enzymatic hydrolysis of lignocellulosic substrates." Current opinion in biotechnology **27**: 150-158.

Mesa, L., N. López, C. Cara, E. Castro, E. González and S. I. Mussatto (2016). "Techno-economic evaluation of strategies based on two steps organosolv pretreatment and enzymatic hydrolysis of sugarcane bagasse for ethanol production." Renewable energy **86**: 270-279.

Miller, G. L. (1959). "Use of dinitrosalicylic acid reagent for determination of reducing sugar." Analytical chemistry **31**(3): 426-428.

Mondal, B. K., S. S. Bandyopadhyay and A. N. Samanta (2017). "Kinetics of CO2 absorption in aqueous hexamethylenediamine." International Journal of Greenhouse Gas Control **56**: 116-125.

Mosier, N., C. Wyman, B. Dale, R. Elander, Y. Lee, M. Holtzapple and M. Ladisch (2005). "Features of promising technologies for pretreatment of lignocellulosic biomass." Bioresource technology **96**(6): 673-686.

Muurinen, E. (2000). Organosolv pulping--A review and distillation study related to peroxyacid pulping. PhD, University of Oulu.

Newton, I. (1676). "Letter to Robert Hooke, February 5, 1676." The Correspondence of Isaac Newton, 1959 **7**: 1661-1675.

Ni, Y. and Q. Hu (1995). "Alcell® lignin solubility in ethanol–water mixtures." Journal of Applied Polymer Science **57**(12): 1441-1446.

Nigam, J. (2001). "Ethanol production from wheat straw hemicellulose hydrolysate by Pichia stipitis." Journal of biotechnology **87**(1): 17-27.

Nitzsche, R., M. Budzinski and A. Gröngröft (2016). "Techno-economic assessment of a wood-based biorefinery concept for the production of polymer-grade ethylene, organosolv lignin and fuel." Bioresource technology **200**: 928-939.

Norlin, L. H. (2000). "Tall oil." Ullmann's Encyclopedia of Industrial Chemistry: Wiley Online Library.

Ochoa-Villarreal, M., E. Aispuro-Hernández, I. Vargas-Arispuro and M. Á. Martínez-Téllez (2012). Plant cell wall polymers: function, structure and biological activity of their derivatives. Polymerization, IntechOpen.

Ogiwara, Y. and K. Arai (1968). "Swelling degree of cellulose materials and hydrolysis rate with cellulase." Textile research journal **38**(9): 885-891.

Parviainen, A., A. W. King, I. Mutikainen, M. Hummel, C. Selg, L. K. Hauru, H. Sixta and I. Kilpeläinen (2013). "Predicting cellulose solvating capabilities of acid–base conjugate ionic liquids." ChemSusChem **6**(11): 2161-2169.

Petrus, L. and C. Petrus-Hoogenbosch (2007). Process for organosolv pulping and use of a gamma lactone in a solvent for organosolv pulping. US Patent 20,070,034,345. United States.

Prat, D., J. Hayler and A. Wells (2014). "A survey of solvent selection guides." Green Chemistry **16**(10): 4546-4551.

Prat, D., O. Pardigon, H.-W. Flemming, S. Letestu, V. r. Ducandas, P. Isnard, E. Guntrum, T. Senac, S. p. Ruisseau and P. Cruciani (2013). "Sanofi's solvent selection guide: a step toward more sustainable processes." Organic Process Research **17**(12): 1517-1525.

Prat, D., A. Wells, J. Hayler, H. Sneddon, C. R. McElroy, S. Abou-Shehada and P. J. Dunn (2015). "CHEM21 selection guide of classical-and less classical-solvents." Green Chemistry **18**(1): 288-296.

Procentese, A., E. Johnson, V. Orr, A. G. Campanile, J. A. Wood, A. Marzocchella and L. Rehmann (2015). "Deep eutectic solvent pretreatment and subsequent saccharification of corncob." Bioresource technology **192**: 31-36.

Quesada-Medina, J., F. J. López-Cremades and P. Olivares-Carrillo (2010). "Organosolv extraction of lignin from hydrolyzed almond shells and application of the δ-value theory." Bioresource technology **101**(21): 8252-8260.

Rabinovich, M., M. Melnick and A. Bolobova (2002). "The structure and mechanism of action of cellulolytic enzymes." Biochemistry **67**(8): 850-871.

Ragauskas, A. J., G. T. Beckham, M. J. Biddy, R. Chandra, F. Chen, M. F. Davis, B. H. Davison, R. A. Dixon, P. Gilna and M. Keller (2014). "Lignin valorization: improving lignin processing in the biorefinery." Science **344**(6185): 1246843.

Richter, G. A. (1932). Acid process of fiber liberation. US Patent 1,880,042. United States.

Richter, J. C. (1949). Process and apparatus for continuous digestion of fibrous materials. US Patent 2,474,862. United States.

Richter, J. C. and O. J. Richter (1965). Continuous process for digesting cellulosic material. US Patent 3,200,032. United States.

Rinaldi, R., R. Jastrzebski, M. T. Clough, J. Ralph, M. Kennema, P. C. Bruijnincx and B. M. Weckhuysen (2016). "Paving the way for lignin valorisation: recent advances in bioengineering, biorefining and catalysis." Angewandte Chemie International Edition **55**(29): 8164-8215.

Rodríguez, A., E. Espinosa, J. Domínguez-Robles, R. Sánchez, I. Bascón and A. Rosal (2018). Different Solvents for Organosolv Pulping. Pulp and Paper Processing, IntechOpen.

Rodríguez, A. and L. Jiménez (2008). "Pulping with organic solvents other than alcohols; Acetone. Amines. Pulp. Paper." Afinidad **65**(535).

Ropars, M., R. Marchal, J. Pourquie and J. Vandecasteele (1992). "Large-scale enzymatic hydrolysis of agricultural lignocellulosic biomass. Part 1: Pretreatment procedures." Bioresource technology **42**(3): 197-204.

Roth, J. A. (1857). Improvement in treating paper stuff. US Patent 17,895. United States.

Sajbrt, V., M. Rosol and P. Ditl (2010). "A comparison of distillery stillage disposal methods." Acta Polytechnica **50**(2).

Santos, R. B., P. Hart, H. Jameel and H.-m. Chang (2013). "Wood based lignin reactions important to the biorefinery and pulp and paper industries." BioResources **8**(1): 1456-1477.

Santos, R. B. and P. W. Hart (2014). "Brownstock washing–A review of the literature." TAPPI Journal **13**(1): 9-19.

Sävelin, P. (2014). "Digester Developments." Valmet Technical Paper Series **1**: 1-18.

Schell, D. J., J. Farmer, M. Newman and J. D. McMillan (2003). "Dilute-sulfuric acid pretreatment of corn stover in pilot-scale reactor." Applied biochemistry biotechnology **105**(1-3): 69-85.

Schuerch, C. (1952). "The solvent properties of liquids and their relation to the solubility, swelling, isolation and fractionation of lignin." Journal of the American Chemical Society **74**(20): 5061-5067.

Seader, J. D., E. J. Henley and D. K. Roper (1998). Separation process principles. New York, John Wiley & Sons.

Seider, W. D., J. D. Seader and D. R. Lewin (2009). Product & Process Design Principles: Synthesis, Analysis and Evaluation, John Wiley & Sons.

Shafiei, M., M. M. Kabir, H. Zilouei, I. S. Horváth and K. Karimi (2013). "Techno-economical study of biogas production improved by steam explosion pretreatment." Bioresource technology **148**: 53-60.

Sholl, D. S. and R. P. Lively (2016). "Seven chemical separations to change the world." Nature News **532**(7600): 435.

Shuai, L. and J. Luterbacher (2016). "Organic solvent effects in biomass conversion reactions." ChemSusChem **9**(2): 133-155.

Shuai, L., Y. M. Questell-Santiago and J. S. Luterbacher (2016). "A mild biomass pretreatment using γ-valerolactone for concentrated sugar production." Green Chemistry **18**(4): 937-943.

Simitzis, J., J. Sfyrakis and A. Faliagas (1995). "Characterization of pore structure by porosimetry and sorption on adsorbents produced from novolac-biomass." Materials chemistry physics **41**(4): 245-250.

Simons, F. L. (1950). "A stain for use in the microscopy of beaten fibers." TAPPI Journal **33**(7): 312-314.

Sluiter, A., B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton and D. Crocker (2008). "Determination of structural carbohydrates and lignin in biomass." NREL Laboratory analytical procedure: NREL/TP-510-42618.

Smith, E. L., A. P. Abbott and K. S. Ryder (2014). "Deep eutectic solvents (DESs) and their applications." Chemical reviews **114**(21): 11060-11082.

Smith, R. E. (2000). Stilbene dyes, Kirk-Othmer Encyclopedia of Chemical Technology, Wiley-Interscience.

Smook, G. A. (1992). Handbook for pulp paper technologist. Peachtree Corners, GA, TAPPI PRESS.

Stewart, J. and A. Thom (1973). "Energy budgets in pine forest." Quarterly Journal of the Royal Meteorological Society **99**(419): 154-170.

Stiefel, S., D. Di Marino, A. Eggert, I. R. Kühnrich, M. Schmidt, P. M. Grande, W. Leitner, A. Jupke and M. Wessling (2017). "Liquid/liquid extraction of biomass-derived lignin from lignocellulosic pretreatments." Green Chemistry **19**(1): 93-97.

Stone, J. and H. Green (1958). "Penetration and diffusion into hardwoods." Pulp & Paper Magazine of Canada **58**(10): 223-232.

Stone, J., A. Scallan, E. Donefer and E. Ahlgren (1969). "Digestibility as a simple function of a molecule of similar size to a cellulase enzyme." Advances in chemistry series **95**: 219-241.

Strazisar, B. R., R. R. Anderson and C. M. White (2001). Degradation of monoethanolamine used in carbon dioxide capture from flue gas of a coal-fired electric power generating station. National Conference on Carbon Sequestration. Washington DC, USA, National Energy Technology Laboratory.

Svensson, S. (1936). Method of and an apparatus for charging cellulose digesters or the like. US Patent 2,029,086. United States.

Swatloski, R. P., S. K. Spear, J. D. Holbrey and R. D. Rogers (2002). "Dissolution of cellose with ionic liquids." Journal of the American Chemical Society **124**(18): 4974-4975.

Tadesse, H. and R. Luque (2011). "Advances on biomass pretreatment using ionic liquids: an overview." Energy & Environmental Science **4**(10): 3913-3929.

Taylor, M. (2012). I Used to Know That: Science: Stuff You Forgot From School. New York, NY, Reader's Digest.

Thakur, V. K., M. K. Thakur, P. Raghavan and M. R. Kessler (2014). "Progress in green polymer composites from lignin for multifunctional applications: a review." ACS Sustainable Chemistry & Engineering **2**(5): 1072-1092.

Thomas, K. V. (1982). Vacuum box for use in high speed papermaking. US Patent 4,359,828. United States.

Tomani, P. (2010). "The lignoboost process." Cellulose Chemistry and Technology **44**(1): 53.

Tomani, P., P. Axegård, N. Berglin, A. Lovell and D. Nordgren (2011). "Integration of lignin removal into a kraft pulp mill and use of lignin as a biofuel." Cellulose Chemistry and Technology **45**(7): 533.

Tran, H. and E. K. Vakkilainen (2008). "The kraft chemical recovery process." TAPPI Kraft Pulping Short Course, https://www.tappi.org/content/events/08kros/manuscripts/1-1.pdf.

Turton, R., R. C. Bailie, W. B. Whiting and J. A. Shaeiwitz (2008). Analysis, synthesis and design of chemical processes. Upper Saddle River, NJ, Pearson Education.

Van Heiningen, A. (2006). "Converting a kraft pulp mill into an integrated forest biorefinery." Pulp & Paper Canada **107**(6): 38-43.

Vazquez-Rojas, R. A., F. J. Garfias-Vásquez and E. R. Bazua-Rueda (2018). "Simulation of a triple effect evaporator of a solution of caustic soda, sodium chloride, and sodium sulfate using Aspen Plus." Computers & Chemical Engineering Journal **112**: 265-273.

Viell, J., A. Harwardt, J. Seiler and W. Marquardt (2013). "Is biomass fractionation by Organosolv-like processes economically viable? A conceptual design study." Bioresource technology **150**: 89-97.

vom Stein, T., P. M. Grande, H. Kayser, F. Sibilla, W. Leitner and P. D. de María (2011). "From biomass to feedstock: one-step fractionation of lignocellulose components by the selective organic acid-catalyzed depolymerization of hemicellulose in a biphasic system." Green Chemistry **13**(7): 1772-1777.

Vroom, K. (1957). "The" H" factor: a means of expressing cooking times and temperatures as a single variable." Pulp & Paper Magazine of Canada **58**: 228-231.

Wallace, G., A. Chesson, J. Lomax and M. Jarvis (1991). "Lignin-carbohydrate complexes in graminaceous cell walls in relation to digestibility." Animal Feed Science and Technology **32**(1-3): 193-199.

Wallberg, O., A.-S. Jönsson and R. Wimmerstedt (2003). "Fractionation and concentration of kraft black liquor lignin with ultrafiltration." Desalination **154**(2): 187-199.

Wang, Q. Q., Z. He, Z. Zhu, Y. H. P. Zhang, Y. Ni, X. L. Luo and J. Y. Zhu (2012). "Evaluations of cellulose accessibilities of lignocelluloses by solute exclusion and protein adsorption techniques." Biotechnology and Bioengineering **109**(2): 381-389.

Watkins, D., M. Nuruddin, M. Hosur, A. Tcherbi-Narteh and S. Jeelani (2015). "Extraction and characterization of lignin from different biomass resources." Journal of Materials Research and Technology **4**(1): 26-32.

White, A. R. and R. M. Brown (1981). "Enzymatic hydrolysis of cellulose: visual characterization of the process." Proceedings of the National Academy of Sciences **78**(2): 1047-1051.

Wildschut, J., A. T. Smit, J. H. Reith and W. J. Huijgen (2013). "Ethanol-based organosolv fractionation of wheat straw for the production of lignin and enzymatically digestible cellulose." Bioresource technology **135**: 58-66.

Woods, N. (1956). "Determination of penetration rates of liquid media into wood using a quarts spiral balance, Part 2." Pulp & Paper Magazine of Canada **57**(4): 142-151.

Worrall, J. J., S. E. Anagnost and R. A. Zabel (1997). "Comparison of wood decay among diverse lignicolous fungi." Mycologia **89**(2): 199-219.

Yáñez-S, M., B. Matsuhiro, C. Nunez, S. Pan, C. A. Hubbell, P. Sannigrahi and A. J. Ragauskas (2014). "Physicochemical characterization of ethanol organosolv lignin (EOL) from Eucalyptus globulus: Effect of extraction conditions on the molecular structure." Polymer Degradation and Stability **110**: 184-194.

Yarbrough, J. M., M. E. Himmel and S.-Y. Ding (2009). "Plant cell wall characterization using scanning probe microscopy techniques." Biotechnology for biofuels **2**(1): 17.

Ye, Y., Y. Liu and J. Chang (2014). "Application of solubility parameter theory to organosolv extraction of lignin from enzymatically hydrolyzed cornstalks." BioResources **9**(2): 3417-3427.

Yu, X., J. L. Minor and R. H. Atalla (1995). "Mechanism of action of Simons' stain." TAPPI Journal **78**(6): 175-180.

Zhang, Z., D. W. Rackemann, W. O. Doherty and I. M. O'Hara (2013). "Glycerol carbonate as green solvent for pretreatment of sugarcane bagasse." Biotechnology for biofuels **6**(1): 153.

Zhang, Z., T. Vancov, S. Mackintosh, B. Basu, A. Lali, G. Qian, P. Hobson and W. O. Doherty (2016). "Assessing dilute acid pretreatment of different lignocellulosic biomasses for enhanced sugar production." Cellulose **23**(6): 3771-3783.

Zhao, X., K. Cheng and D. Liu (2009). "Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis." Applied microbiology and biotechnology **82**(5): 815.

Zhao, X., L. Zhang and D. Liu (2012). "Biomass recalcitrance. Part I: the chemical compositions and physical structures affecting the enzymatic hydrolysis of lignocellulose." Biofuels, Bioproducts and Biorefining **6**(4): 465-482.

Zheng, Y., Z. Pan and R. Zhang (2009). "Overview of biomass pretreatment for cellulosic ethanol production." International journal of agricultural and biological engineering **2**(3): 51-68.